FINAL REPORT
PREPARED BY
THE CAMBRIAN ENGINEERING GROUP LIMITED

FOR

CARBOVAN INC.
FOR SUBMISSION TO
SUPPLY AND SERVICES CANADA
HULL, QUEBEC

ON

FLUIDIZED-BED CATALYTIC CRACKING (FCC) CATALYST FABRICATION-FINAL REPORT

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1.0 EXECUTIVE SUMMARY

Carbovan is constructing a plant in Fort McMurray, Alberta to extract vanadium and other valuable materials from flyash produced by Suncor. A by-product of the extraction is a leach residue which has been reported by the Ontario Research Foundation to contain as much as 95% of zeolitic material (Appendix II, Progress Report #1).

Preliminary tests in 1986 on the leach residue for catalytic cracking activity indicated that the residue had good potential as a low cost fluidized-bed catalytic cracking (FCC) catalyst.

Carbovan therefore, submitted an unsolicited proposal that was accepted by CANMET of Energy, Mines and Resources. The overall purpose of the project was to evaluate the usefulness of the leach residue by-product in a number of applications, and in particular as an FCC catalyst.

A literature search on the properties and uses of zeolites was conducted. Zeolites are generally used on a commercial basis as high purity specialty chemicals. Synthetic zeolites are preferred over natural zeolites because they are prepared under carefully controlled conditions. The zeolite specifications for the main industrial applications, such as detergents, catalysts, adsorbents and fillers, were prepared, together with the market trends for these products. In general, zeolite usage is expected to increase at a rate of about 5%/year. However, the market is extremely competitive.

The leach residue was characterized and the properties compared to the specifications of the industrial products. The physical properties of the residue such as particle size, surface area, pore diameter and pore volume, indicated that the residue would not be suitable for use in detergents, catalysts and microsieves. However, it appeared to be suitable as a filler material.

From a chemical point of view, the high metals content of the residue also indicated that it would not perform well in detergent, catalyst and microsieve applications. Moreover, the metals might cause problems when the residue is used as a filler. In addition, the zeolite phase did not have the faujasite structure that is commonly present in these three applications.

1.0 EXECUTIVE SUMMARY (Cont'd)

The leach residue was tested in the above four applications. The experimental results generally agreed with the predictions made from comparing the properties of the residue with the specifications of the commercial products. Thus, the residue displayed very little capacity to adsorb ions that cause water hardness, low activity for cracking, and weak affinity for water during microsieve testing. However, the residue performed as well as a commercial filler in tests with polypropylene. This application should be investigated further. However, the filled polymer was not as thermally stable as the unfilled counterpart due presumably to the metals in the residue.

The leach residue possesses catalytic activity. However, in its present form it cannot compete with commercial FCC catalysts that are twice as active. The literature survey, analytical work and experimental results of this project clearly indicate the extensive chemical and physical changes to the residue that will be required to make it competitive from a reaction point of view. These changes are much more extensive than was originally envisioned and fall well beyond the scope of this project. Carbovan therefore, decided to cancel the original residue modification work since only marginal improvements in activity could have been expected.

2. INTRODUCTION

2.1 Historical

The Carbovan extraction process for recovering vanadium and carbon from waste flyash originating from the powerhouse at Suncor Incorporated in Fort McMurrary, Alberta, was developed from research work conducted at the Ontario Research Foundation (ORF) in Mississauga, Ontario. A by-product of the extraction process is a leach residue reportedly containing up to 95% of zeolitic material (Appendix II, Progress Report #1).

Since zeolites are extensively used in the petroleum industry for the manufacture of fluidized-bed catalytic cracking (FCC) catalysts, preliminary testing was conducted in early 1986 by the Saskatchewan Research Council (SRC) in Regina, Saskatchewan to evaluate the potential of using the leach residue as a source of low cost FCC catalyst. A copy of the SRC report is included in Appendix I.

Based on the positive results of the preliminary tests and the favourable comments contained in the SRC report, Carbovan worked with ORF and SRC to submit a proposal to CANMET of Energy, Mines and Resources, Energy Research Laboratories in Ottawa, Ontario. The proposal was accepted by CANMET and contract number 23440-7-9124/01-SQ was awarded to Carbovan by Supply and Services Canada (DSS) in Hull, Quebec. The total cost of the proposal was estimated at $169,600, with $84,800 to be paid by DSS and an equivalent amount by Carbovan.

2.2 Project Team

The Cambrian Engineering Group Limited (Cambrian) in Mississauga, Ontario was selected to manage the project. ORF was responsible for preparation, characterization, evaluation and modification of the zeolite leach residue. SRC was responsible for evaluating the catalytic performance of the leach residue with respect to the conversion of gas oil to gasoline.

2.3 Project Objectives

The overall objective of the project was to evaluate the potential of the leach residue by-product from Carbovan's extraction process. Since the leach residue contains zeolite material, a number of industries that are significant users of zeolite were investigated. Of particular interest was use of the leach residue as a low cost FCC catalyst.

Accordingly, the main goals of the project were:

(1) to provide a summary report on the properties of the leach residue and the preliminary catalytic evaluation test conducted by SRC;

(2) to determine the specifications of currently available zeolite products that are used in soap detergent, FCC catalyst, molecular sieve and plastic filler applications;

(3) to evaluate the physical and chemical properties of the unmodified leach residue;

(4) to evaluate the catalytic properties of the unmodified leach residue;

(5) to conduct preliminary evaluation of the unmodified leach residue for alternate uses, such as soap detergent, molecular sieve and plastic filler applications;

(6) to modify the leach residue via dilution and doping in order to improve its catalytic properties;

(7) to evaluate the catalytic properties of the resultant modified leach residue; and

(8) to prepare a final report on the above work for CANMET and DSS (Department of Supply and Services).

2.4 Project Execution

The project was scheduled to commence on July 15, 1987. However, as a result of delays, work on the project did not officially commence until October 7, 1987. As a result, a contract amendment was submitted to extend the due date by 4 months to June 30, 1988. Additional turn of events have served to delay the preparation of the Final Report.

The first 5 goals of Section 2.3 have been accomplished. The main results will be presented and discussed in the next section. Based on the results obtained in accomplishing the above 5 goals, experimental work was terminated and the tasks involved in goals 6 and 7 were not carried out. The reasons for the decision will also be presented in the next section.

3. RESULTS AND DISCUSSION

In this section, the main results will be presented and discussed. These results will be drawn from the following reports that are included in the appendices.

Appendix I	-	SRC	-	Zeolite Material for Catalyst Testing
Appendix II	-	ORF	-	Fabrication of FCC Catalysts from Suncor Flyash Leach Residue
Appendix III	-	SRC	-	Carbovan FCC Catalyst Fabrication Project

3.1 Summary Report

A primary objective of the Carbovan extraction process is the recovery of vanadium. Therefore, the extraction process was optimized to minimize potential vanadium losses to the leach residue. Possible exchange of the dissolved vanadium with other cations in the leach residue and post precipitation of vanadium compounds were therefore investigated.

In order to identify such losses of vanadium to the leach residue, the residue was examined by x-ray diffraction (XRD) to determine small amounts of calcium vanadate. Numerous intense peaks were obtained (Progress Report No. 1 of Appendix II), making it difficult to detect the weak peaks for calcium vanadates. In spite of this, it was concluded that no positive evidence was found for the presence of calcium metavanadate $Ca(VO_3)_2$ or calcium pyrovanadate ($Ca_2V_2O_7$). However, it was estimated that these compounds would have to be present in a well crystallized form and in concentrations exceeding about 2 weight % before they could be detected.

From the XRD patterns, the major crystalline phases in the leach residue from two different leach conditions were identified as follows:

3.1 Summary Report (Cont'd)

MAJOR PHASES OF LEACH RESIDUE USED IN PRELIMINARY TESTS

Phase		Leach Residue	
		$NaOH/Na_2CO_3$	NaOH
Analcime	$NaAlSi_2O_6.H_2O$	90%	20%
Zeolite	$Na_3Al_3Si_5O_{16}.16H_2O$	5%	75%
Other		5%	5%
TOTAL		100%	100%

The FCC preliminary tests were conducted by SRC in early 1986 (refer to Appendix I). The test used was the Fluidized-Bed Cracking Catalysts by Microactivity Test (FCC MAT). The technique employed was based on the ASTM D 3907-80 FCC MAT procedure (Appendix I). The only deviation from the ASTM procedure was the use of two temperatures (482 and 504C), rather than one.

The purpose of the preliminary tests was to measure the conversion of a gas oil feedstock (boiling range 345 to 525C) to gasoline (boiling point less than 216C). The feedstock used was a gas oil derived from a conventional light crude. The only exception to this was in test number 5 when gas oil derived from a synthetic crude was utilized. The results were as follows:

3.1 Summary Report (Cont'd)

PRELIMINARY CATALYTIC TESTING OF LEACH RESIDUE BY FCC-MAT

Test No.	Residue Sample	Residue Treatment	Reaction Temp (C)	Conversion of Gas Oil to Gasoline (wt %)	Gas (ml)
1	1P	As Received	482	43.4	40
2	1P	Decoked	482	20.7	11
3	2P	Dried	482	41.1	97
4	2P	Dried	504	47.7	109
5	2P	Diluted with Sand	482	61.0	62
6	3P	As Received	482	40.0	64

Three samples of leach residue were used in the above preliminary tests:

Sample 1P - dried leach residue, and
Sample 2P - wet leach residue, and
Sample 3P - pretreated leach residue

These residues were produced from a caustic leach and originated from either ESP flyash or a 1:1 BH:ESP flyash mixture.

The typical FCC catalyst must first be decoked in a furnace at 590C for 3 hours before being tested. A portion of Sample 1P was therefore decoked. Comparison of the weight percent conversion to gasoline for test numbers 1 and 2 indicated a lower catalytic activity for the decoked residue. All remaining tests were therefore carried out without decoking.

3.1 Summary Report (Cont'd)

Comparison of test number 3 with the results of test number 1 indicated very little difference in conversion to gasoline. Therefore drying of the leach residue did not adversely affect product formation. The untreated third sample of leach residue also gave similar conversion (test number 6).

Characterization of the leach residue by ORF (Progress Report No. 1 of Appendix I), indicated a mean particle size of around 12 microns for the leach residue. This is small compared to 70 microns for a typical commercial catalyst. Small particle size could cause problems with the FCC MAT unit since packing of the particles during the test would result in the gas oil not being exposed to sufficient catalytic surface. This problem was indicated by higher than normal pressure drops across the reactor.

Therefore, for test number 5, the leach residue was mixed with some sand in order to prevent packing. The conversion rate was significantly improved from 40% to 61%.

Under similar test conditions, the conversion rate for a commercial catalyst is around 60 to 70%. Therefore, from a conversion point of view, the zeolite material in the leach residue had significant potential as an FCC catalyst. However, the gas made from the leach residue varied from a low of 40 ml to a high of 109 ml. This is quite high compared to 40 to 50 ml for a typical commercial catalyst. Gas analysis on test number 6 indicated a H_2/CH_4 ratio of approximately 3, compared to 0.5 to 1.0 for a commercial catalyst. Therefore, some undesirable dehydrogenation reaction took place. It was felt that the dehydrogenation problem could be overcome by additional development work on the zeolite material in the leach residue.

Thus, the possibility of developing the leach residue into a low cost FCC catalyst was very attractive. By simply mixing the residue with sand, a conversion rate similar to that for natural clays (bentonite), but slightly less than for available commercial catalysts, was obtained. With such a material, further improvements might provide comparable performance to commercial catalysts. An incentive for conducting a more systematic and thorough evaluation of the leach residue clearly existed.

3.2 Specification Analysis

Specifications and market data for the most important zeolite products were gathered by ORF (Section 2 of Appendix II). The specifications serve as bench marks for evaluating the leach residue produced by Carbovan while the market data provide information on the economic viability of commercializing the production of zeolite products based on the by-product residue.

In this section, the information collected by ORF will be summarized, starting with background information on zeolites and leading to commercial zeolites in detergent, catalyst, microsieve and filler applications.

3.2.1 Background Information on Zeolites

The term zeolite describes a large and expanding group of crystalline aluminosilicates whose origins lie as natural occurring materials. Today however, they are more often found as synthetically produced hybrids.

Zeolites are crystalline microporous solids containing cavities and channels of molecular dimensions (3 to 10 Angstroms). As such, they are often called molecular sieves. Although zeolites are based on aluminosilicate chemistry, recent developments in alumino-phosphate chemistry have expanded the composition to include more than 13 elements besides the traditional Si, Al, Ga, Ge and Fe.

Structurally, zeolites are based on an infinitely extending, three dimensional network of AlO_4 and SiO_4 tetrahedra that are linked by the sharing of oxygen atoms. Many theoretical structures are possible but only the thermally and chemically stable ones have industrial importance.

The chemical formula of a crystallographic unit cell of a zeolite can be expressed in terms of the oxides:

$$M_{x/n}\ (\ (AlO_2)_x\ (SiO_2)_y\ )\quad mH_2O$$

3.2.1 Background Information on Zeolites (Cont'd)

where M is a cation of valence n and m is the number of water molecules. The framework contains channels and interconnecting voids which are occupied by cations and water molecules. The cations are usually mobile and can be replaced/exchanged with other cations.

The molecular control of ingress and egress to reactive sites, as well as control of the size of the site itself, facilitates molecular control of chemical reactions. This allows significant molecular engineering of molecules that are less than 10 Angstroms in size.

Zeolites may occur naturally in the environment, usually as deposits of altered volcanic ash. The major areas of application for natural zeolites are as follows:

(1)	Ion Exchange	-	agriculture
		-	water treatment
		-	radioactive waste clean up
(2)	Water Adsorption	-	desiccation
		-	heat storage
(3)	Gas Adsorption	-	odor control
		-	gas purification
(4)	Animal Feed	-	feed supplement
(5)	Paper	-	filler material.

Of the above areas of application, the first three are most important. However, despite the versatility and market potential of natural zeolites, they have yet to meet customer acceptance in most market areas. The most important natural zeolites (see also Table 1 of Appendix II) are listed below:

3.2.1 Background Information on Zeolites (Cont'd)

IMPORTANT ZEOLITES THAT ARE FOUND NATURALLY

Group No.	Group Description	Zeolite Name	Void Volume (%)	Specific Gravity	Ion Exchange Capacity (meq/g)
1	Single 4-Ring	Analcime	18	2.24 to 2.29	4.54
		Phillipsite	31	2.15 to 2.20	3.87
		Laumonite	34	2.20 to 2.30	4.25
2	Single 6-Ring	Erionite	35	2.02 to 2.08	3.12
3	Double 4-Ring	A (Linde)	47	1.99	5.48
4	Double 6-Ring	Chabazite	47	2.05 to 2.10	3.81
5	Complex 4-1	Natrolite	23	2.20 to 2.26	5.26
6	Complex 5-1	Mordenite	28	2.12 to 2.15	2.29
7	Complex 4-4-1	Clinoptilolite	34	2.16	2.54

It should be noted that analcime was one of the major zeolite phases identified in the leach residue (Section 3.1).

Synthetic zeolites are high purity specialty chemicals. They are prepared under closely controlled conditions. The most important commercially available synthetic zeolites are listed below:

3.2.1 Background Information on Zeolites (Cont'd)

COMMERCIALLY AVAILABLE SYNTHETIC ZEOLITES

Zeolite Name	Pore Size (Angstroms)	Si/Al Ratio	Cation
Faujasite - X	7.4	1.0 to 1.5	Na
Faujasite - Y	7.4	1.5 to 3.0	Na
Faujasite - US -Y	7.4	> 3.0	H
Faujasite - A	3	1.0	K, Na
Faujasite - A	4	1.0	Na
Faujasite - A	4.5	1.0	Ca, Na
Chabazite	4	4.0	"N"
Clinoptilolite	4 x 5	5.5	"N"
Erionite	3.8	4.0	"N"
Ferrierite	5.5 x 4.8	5.0 to 10.0	H
L-Type	6	3.0 to 3.5	Na, H
Mazzite	5.8	3.5	Na, H
Mordenite	6 x 7	5.5	"N"
Mordenite	6 x 7	5.0 to 6.0	Na
Mordenite	6 x 7	5.0 to 10.0	H
Offretite	5.8	4.0	K, H
Phillipsite	3	2.0	"N"
Silicalite	5.5	-	H
ZSM - 5	5.5	10.0 to 500.0	H

3.2.1 Background Information on Zeolites (Cont'd)

It should also be noted that, although analcime was listed as one of the important natural zeolites, it was not included in this list of commercially available synthetic zeolites. Common to both lists are the following zeolites: A, chabazite, clinoptilolite, erionite, mordenite and phillipsite.

The major fields of application of synthetic zeolites are:

(1)	Detergent Builder	-	Sodium tripolyphosphate substitute
(2)	Catalyst Cracking	-	FCC
		-	fixed bed
(3)	Microsieve	-	desiccation
		-	gas purification

The largest consumption of synthetic zeolites is in detergents, with 80 to 90% of worldwide sales going into this application. However, usage in the U.S. market is not as high due to preference in alternative chemistry. The second largest market for synthetic zeolites (accounting for 10 to 15%) is in catalyst formulation for the petrochemical industry. Finally, 5 to 10% of total zeolite production is employed in adsorbent applications.

3.2.2 Detergent Application

3.2.2.1 Background on Detergents

The main conventional water softeners used in detergent powder and cakes is sodium tripolyphosphate (STPP). However, STPP poses serious environmental problems because it promotes rapid development of algae. The algae in turn are deleterious to water fauna and they also foul the effluent treatment plant.

Some zeolites possess an inherent ability to exchange mobile sodium and potassium cations for calcium and magnesium cations which are mainly responsible for water hardness. Thus, by optimizing the detergent formulation, close to 99% of the dissolved calcium and magnesium can be removed by adsorption on the zeolite.

It is believed that as legislation "banning" STPP comes into effect, even more zeolite will be used to replace STPP.

3.2.2.2 Zeolite Specifications

Natural zeolites are not suitable for detergent applications. Their particle size is not optimal, and the presence of heavy metal ions could catalyze decomposition of other components in the detergent. Synthetic zeolite A satisfies the requirements of particle size, purity, and core exchange capacity and rate. For these reasons, synthetic zeolite A, or a proprietary version of it, has been selected for use by the detergent industry.

Zeolite A removes hardness by ion exchange, rather than by chelation associated with STPP. Most of the ion exchange capacity of zeolite 4A exists within the 11.4 Angstrom cavities that are accessed through 4.2 Angstrom openings. The pores permit passage of calcium ions into the cavities where they exchange with the sodium ions. However, magnesium ions have an effective ionic radius that is larger than 4.2 Angstroms, and therefore do not pass as easily through the openings. Thus, STPP or other non-phosphate compound might be required to assist in the magnesium ion uptake.

Based on zeolite A, the specifications for a zeolite that is suitable for detergent application is summarized as follows:

SPECIFICATIONS OF ZEOLITE FOR DETERGENTS

PARAMETER	DESCRIPTION
Zeolite	Dried, powdered, crystalline product of aluminate, silicate, and caustic reaction in aqueous solution.
Appearance	Fine "white" pure powder.
Moisture Content	18 to 22%
Aluminum Content	18.0% minimum (anhydrous basis)
Elemental Ratio Na:Al:Si	0.9 to 1.1 : 0.9 to 1.1 : 0.9 to 1.1

3.2.2.2 Zeolite Specifications (Cont'd)

SPECIFICATIONS OF ZEOLITE FOR DETERGENTS (Cont'd)

PARAMETER	DESCRIPTION
Phase Composition	Type A zeolite - 85% minimum (vs. Standard Sample) Hydroxysodalite - 5% maximum (vs. Standard Sample) Crystalline Quartz - 1% maximum
Particle Size	Individual Crystal - 6 microns maximum Mean Particle Size - 4 microns maximum Particles less than 1 micron - 10% maximum
Calcium Exchange Capacity	255 mg $CaCO_3$/g dry zeolite minimum
Causticity (as Na_2O)	1.5% maximum
pH (1% slurry)	10.1 to 11.1
Dissolved Metal Ion	<200 ppm

The advantages of zeolite A over STPP are:

(1) The fine particle size (4 microns maximum) of the zeolite enables it to be incorporated directly into the detergent formation. It is also effectively washed out during "rinsing".

(2) It provides a combination of high ion exchange capacity (255 mg $CaCO_3$/g zeolite minimum) with strong binding force for the metallic ions that cause water hardness.

(3) Unlike STPP, it does not cake during storage.

3.2.2.2 Zeolite Specifications (Cont'd)

(4) It reduces sticking of the formulation due to its high moisture holding capacity.

(5) It is cheaper than STPP.

(6) It is an odorless, free flowing, white powder that, as mentioned above, does not pose an environmental problem.

3.2.2.3 Market Trends

The major world markets in 1986 for detergent grade zeolites is shown below:

1986 MAJOR WORLD MARKET USAGE AND CAPACITY FOR DETERGENT GRADE ZEOLITES

MARKET	USAGE (tpa)	CAPACITY (tpa)
Europe	190,000	205,000
Japan	100,000	110,000 to 150,000
U S A	70,000	140,000

Growth in zeolite usage by the detergent industry is expected for the three major world markets during the early 1990's. In Europe the market is expected to exceed 500,000 tpa based on the assumption that most countries will ban the use of STPP. As a result, major producers are expanding detergent zeolite production, especially the synthetic A forms. Similarly, the Japanese market is expected to increase to 150,000 tpa. There is currently an over-supply of zeolite A in both markets.

3.2.2.3 Market Trends (Cont'd)

The U.S.A. market is less predictable because only 25% of the U.S. states have banned STPP, and Procter and Gamble now uses alternative chemicals rather than zeolites. However, the market is expected to increase significantly due to the competitive price of zeolite A over alternative water softening materials.

3.2.3 Catalyst Application

3.2.3.1 Background on Zeolite Catalysts

The four major mechanisms that explain zeolite catalyst activity are:

(1) Hydroxyl groups in the zeolite framework release hydrogen ions to the reactant.

(2) The electrostatic field of the zeolite rearranges the atomic bands of the reactant.

(3) The metallic cations in the zeolite structure catalyze the reaction.

(4) Holes, caused by missing oxygen atoms of the zeolite lattice, result in catalytic sites with a net positive charge.

The above properties of the zeolites are responsible for selective reactions in which certain carbon linkages are altered while others remain intact. In addition, molecules are selectively excluded from the reactions if their size and shape do not allow them to pass through the zeolite pore opening to the catalyst site.

Reactions taking place in zeolites are heterogeneous in nature, and catalysts formulated from zeolites are usually of the fluidized or fixed bed type. The main processes that utilize zeolite catalysts are summarized in the following sections.

3.2.3.2 Fluidized-Bed Catalytic Cracking (FCC)

In the FCC process, heavy petroleum fractions are converted to lighter boiling gasoline and light fuel oils. Liquefied petroleum gas (LPG), heavy fuel oil, and coke are the major by-products. The FCC process is optimized to provide the highest yield of high octane gasoline while suppressing the formation of by-products.

Zeolite X (faujasite doped with rare earth metals) was the initial catalyst used in gasoline production. It has been superseded by zeolite Y which has a higher SiO_2/Al_2O_3 ratio and lower acidity.

Higher silica faujasite zeolites are being achieved through improvements in synthetic processing technology. With an increased SiO_2/Al_2O_3 ratio and resultant decrease in acid site density, a more selective catalyst is obtained for the production of high octane olefins with reduced product cracking and hydrogen transfer. ZSM-5 catalyst can also be included to selectively convert low octane paraffins to high octane components.

3.2.3.3 Hydrocracking

The second largest catalyst application for zeolites involves hydrocarbon cracking under high hydrogen partial pressures whereby hydrogen is added to the product. Elevated temperatures and pressures are employed. The large pore zeolites, X, Y, and mordenite, are favoured due to their long lifetime (up to six years) and resistance to contaminants containing sulfur and nitrogen.

High silica faujasites are also preferred when heavy oil feeds are used.

3.2.3.4 Isomerization and Selective Cracking

Due to the increased octane requirements in gasoline resulting from the removal of tetraethyl lead from the formulation, considerable effort has been expended to improve pentane and hexane isomerization capacity in refineries. A mordenite type zeolite with platinum inclusion is the typical catalyst used. In the past four years, about 20% of all refinery capital expenditures were spent on installing and upgrading isomerization systems.

3.2.3.4 Isomerization and Selective Cracking (Cont'd)

Catalytic LPG production from pentane and hexane is known as selectoforming. High temperatures and pressures (with high hydrogen/hydrocarbon ratios) are involved. Erionite type zeolites were originally used until improvements to the process for direct conversion of paraffin to high octane gasoline using ZSM-5 zeolite was made by Mobil in the mid 1970's.

Two other important selectoforming processes are the conversion of light hydrocarbons to monocyclic aromatics (a high temperature process) and olefins to gasoline and distillates (low temperature processing). In both cases, ZSM-5 is the catalyst. In the first process, the medium sized pore inhibits coke formation, and in the second, the shape selectivity of the catalyst allows production of high quality jet fuels.

3.2.3.5 Synfuel Production

The processes of interest are:

(1) Methanol to Gasoline

Natural gas can be converted directly to liquid fuels by the MTG process. The ZSM-5 zeolite catalyst is of critical importance to the process due to its ideal medium pore size. A smaller pore size would produce no aromatics, while a larger pore zeolite would deactivate rapidly. The MTG process is being utilized in a New Zealand plant.

(2) Ethanol to Gasoline

The production of gasoline from fermentation products has been investigated using ZSM-5 zeolite. The process is similar to (1) above. However, in this case ethanol, diluted by other fermentation products, is the starting material.

(3) Fischer-Tropsch Process

The Fischer-Tropsch process involves the conversion of carbon monoxide and hydrogen to liquid hydrocarbon products in the form of straight chained paraffins and olefins. These products are readily converted to gasoline by the ZSM-5 catalyst. However, the Fischer-Tropsch process is expensive and industrial development has been pursued only by South Africa.

3.2.3.6 Other Petrochemical Processes

A list of other minor petrochemical processes that utilize zeolites is given below:

LIST OF MINOR PETROCHEMICAL PROCESSES USING ZEOLITES

PETROCHEMICAL PROCESS	ZEOLITE
Toluene Disproportionation	Zeolite X, ZSM-5
Methanol to Olefins	ZSM-5, SAPO Linde
Toluene Alkylation	Faujasite, ZSM-5
Para-selective Processing - (Toluene, Styrene)	ZSM-5
Xylene Isomerization	ZSM-5
Distillate Dewaxing	ZSM-5, Mordenite

In all the above processes, the zeolites are modified with the addition of Pt, Pd and rare earth cations by means of proprietary processes.

3.2.3.7 NO_x Gas Treatment

Future conversion of noxious NO_x gas to nitrogen from a variety of industrial sources will likely involve zeolite catalysts. Mordenite and/or Y zeolites have been proven to promote conversion of NO and NO_2 to nitrogen. The application of the process is already being made in new European power plants where flue gas emissions are closely controlled. It is likely that this will be a high growth area for zeolite applications.

3.2.3.8 Zeolite Specifications

The zeolites used as catalysts in industrial applications are summarized below:

ZEOLITE CATALYSTS USED IN INDUSTRIAL PROCESSES

PROCESS	ZEOLITE	PRODUCT
Catalytic Cracking	Faujasite	Gasoline, Fuel Oil
Hydrocracking	Faujasite	Kerosene, Jet Fuel Benzene, Toluene, Xylene
Hydro-isomerization	Mordenite	iso-Hexane, Heptane (octane enhancer)
iso/n-Paraffin Separation	Ca-A	Pure n-Paraffins
Dewaxing	ZSM-5, Mordenite	Low Pour Point Lubricants
Olefin Drying	K-A	Polyolefin Feed
Benzene Alkylation	ZSM-5	Styrene
Xylene Isomerization	ZSM-5	para-Xylene

Since pore size is very important to the process involved, the zeolite catalysts have been accordingly classified.

3.2.3.8 Zeolite Specifications (Cont'd)

CLASSIFICATION OF ZEOLITE CATALYSTS BY PORE SIZE

PORE SIZE CLASSIFICATION	ZEOLITE		PORE SIZE (Angstroms)
Large Pore	Faujasite -	Linde Type X	7.4
	-	Linde Type Y	7.4
	Mordenite		2.9 x 5.7 6.7 x 7.0
	Type L		7.1
Medium Pore	ZSM-5		5.4 x 5.6 5.1 x 5.6
	Synthetic		3.4 x 4.8
	Ferrierite		4.3 x 5.5
Small Pore	Erionite		3.6 x 5.2

The chemical and physical properties of a high alumina clay and XZ-2 zeolite FCC catalyst are summarized below. Values for both fresh and equilibrium catalysts are given. Further details can be found in Appendix II.

3.2.3.8 Zeolite Specifications (Cont'd)

PROPERTIES OF FRESH AND EQUILIBRIUM FCC CATALYST

PROPERTY	AMORPHOUS HIGH ALUMINA		ZEOLITE XZ-2	
	FRESH	EQUIL	FRESH	EQUIL
Chemical Analysis (Dry Basis Wt %):				
Aluminum	28	21.5	31	25.4
Carbon	0	0.2	0	0.3
Sulfate	0.7	0.1	0.3	0.1
Sodium	0.03	0.03	0.04	0.04
Iron (ppm)	300	3900	700	3700
Metals (ppm V+Ni+Cu)	0	162	0	259
Physical analysis:				
Surface Area (m^2/g)	415	140	335	97
Pore Volume (cm^3/g)	0.88	0.43	0.60	0.45
Bulk Density (g/cm^3)	0.39	0.70	0.52	0.68
Particle Size (Micromesh Sieves Wt %):				
0 to 20 microns	2	0	2	0
0 to 40 microns	17	8	19	6
0 to 80 microns	68	69	75	75
Average (microns)	65	63	62	62
Catalytic Activity (Microactivity):				
Vol % Conversion	60	59	85	73

3.2.3.8 Zeolite Specifications (Cont'd)

It should be noted that, by comparing the analytical results for the fresh and equilibrium catalysts, major physical and chemical changes occurring in the FCC catalyst during use can be observed. For example, there was an extremely large increase in the iron and metals content. Also, the surface area for both catalysts decreased to about one third the area of the fresh catalyst. Other properties such as particle size, showed very little change.

3.2.3.9 Market Trends

The world consumption of zeolite catalyst by market and process is given below:

WORLD CONSUMPTION OF ZEOLITE CATALYSTS

PROCESS	CONSUMPTION (METRIC TONNES PER YEAR)			
	U.S.	EUROPE	OTHER	TOTAL
Catalytic Cracking	165,000	50,000	85,000	300,000
Hydrocracking	1,300	300	1,100	2,700
Synfuels	-	-	100	100
Other Petroleum Processes	600	300	200	1,100
Petrochemicals	< 200	< 200	< 100	< 500
NO_x Reduction	-	< 200	< 300	< 500
TOTAL	167,100	51,000	86,800	304,900

This table shows that more than half of the zeolite catalysts are consumed in the U.S. and that catalytic cracking is by far the major user of these catalysts. The above catalyst consumption has a market value of around 700 million dollars.

3.2.3.9 Market Trends (Cont'd)

There are two major trends in the demand for cracking catalysts. Firstly, although the largest market (FCC catalysts) is maturing, a 3 to 5% growth rate is predicted for the next 2 to 3 years. Little growth, however, is seen for the hydrocracking catalyst market, as the incentive to process heavy crudes diminishes with the price difference between light and heavy crudes. Less demand for hydrocracking catalysts could result.

The second trend is the increased production of high octane unleaded gasoline and the parallel increased demand for, and research into, Y type zeolites. The major interest is in the production of new stable catalysts, rather than enhancement of the already exceptional catalytic properties of these zeolites.

There exists an overcapacity for FCC zeolites in the western markets. The competition is therefore lively, but the market is generally stable. Catalyst producers are thus now promoting more specialized "value added" types of materials in new technology areas, such as synfuels and NO_x abatement systems.

The new bulk market to develop will likely be in South America where residual cracking is more commonplace and higher catalyst loadings are required.

In general, the large majority of petrochemical catalysts are manufactured under strictly controlled process conditions. Raw materials are either synthetically produced high purity materials, or they are naturally occurring mineral phases that have been pretreated to remove non-beneficial impurities. Petrochemical catalysts, therefore, are produced mainly from synthetic zeolites, thus allowing for tighter quality control.

3.2.4 Microsieve Application

3.2.4.1 Background on Microsieves

Zeolites are well suited to application as molecular adsorbents because of their microporous crystalline nature. They have the ability to be highly selective, to have high adsorption capacity, and to be stable especially during regeneration.

3.2.4.1 Background on Microsieves (Cont'd)

The selectivity of the zeolite adsorbent is dependent largely on pore size. Some degree of flexibility in the zeolite structure is possible by ion exchange modification of the basic unit cell. This allows some tailoring of the pore size to suit the application. Thus, highly selective adsorbents could be manufactured by careful adjustment of the polar properties as well as the final pore size of the zeolite.

The equilibrium selectivity of zeolites is determined by two major factors:

(1) The Van der Waals forces acting on the sorbent surface, and

(2) The degree of polarity on the sorbent surface.

Van der Waals forces tend to be significant only on homogeneous non-polar surfaces of high silica zeolites. The effect is proportional to the size of the adsorbed molecule. For example, in the sorption of n-hexane from benzene, the n-hexane is precisely the right fit for the ZSM-5 structure and the Van der Waals interaction will be at a maximum between n-hexane and the zeolite.

On the other hand, due to the presence of exchangeable cations in zeolites, polar molecules such as H_2O, N_2 and CO_2 have a higher affinity for adsorption than nonpolar species. The affinity increases with cation charge and decreases with cation radius. There is a direct relationship between the change in polar strength of the adsorbent and the change in microsieve selectivity. This type of selectivity explains the affinity for unsaturated hydrocarbons over paraffins by zeolites of high silica/alumina ratio.

The adsorption process itself is dependent on three other factors:

(1) The phase of the sorption process (gas or liquid),
(2) The method by which the adsorbent is regenerated, and
(3) The contacting scheme.

With regard to the phase, low temperature gas phases are favoured over high temperature liquid separations due to advantages in energy consumption, sorption rate and unwanted side reactions.
For regeneration of the adsorbent, four methods are common:

(1) Pressure modulation,
(2) Temperature shift,
(3) Displacement with a competitive adsorbate, and
(4) Purging with an inert phase.

3.2.4.2 Zeolite Specifications

A list of the purification processes that utilize zeolite adsorbents, together with the phase employed is given below:

PURIFICATION PROCESSES WITH ZEOLITE ADSORBENTS

PROCESS	FEED	PHASE	ADSORBENT
Drying	Natural Gas	Gas	4A
	Air	Gas	4A
	Refrigerants	Gas/Liquid	4A (modified)
	Cracked Gas	Gas	3A
	Organic Solvents	Liquid	3A
	Acid Gas	Gas	Chabazite
CO_2 Removal	Air in Submarines/ Aircraft	Gas	4A
H_2S Removal	Sour Gas	Gas	Ca-A, Ca-Chabazite
SO_x and NO_x Removal	Air	Gas	Silicalite
Kr^{85} Removal	Air	Gas	Silicalite, H-Mordenite
I^{129} Removal	Air	Gas	Ag-X,Ag-Mordenite
Alcohol Concentration	Aqueous Alcohol	Liquid	3A, 4A

A similar list for bulk separation processes of components in a mixture is also given:

3.2.4.2 Zeolite Specifications (Cont'd)

BULK SEPARATION PROCESSES USING ZEOLITE ADSORBENTS

PROCESS	FEED	PHASE	ADSORBENT
Linear Paraffin Separation:			
-Isoslv	C_6 to C_{10} Distillate	Gas	5A
-BP		Gas	5A
-TSF	C_{10} to C_{16} Kerosene	Gas	5A
-Ensorb	C_{10} to C_{16} Kerosene	Gas	5A
-Elf-N-Iself	Light Naphtha	Gas	5A
-Molex	Kerosene	Liquid	5A
Aromatics Separation:			
- Parex	C_8 Aromatics	Liquid	Sr-Ba-X
- Ebex	C_8 Aromatics	Liquid	Sr-K-X
Olefins from Paraffins:			
- Olex	C_4 Distillate	Liquid	-
Air Separation:			
- O_2 Production	Air	Gas	5A, 13X
- N_2 Production	Air	Gas	4A
Monosaccharide Separation:			
- Sarex	Corn Syrup	Liquid	Ca-Y

3.2.4.2 Zeolite Specifications (Cont'd)

Separation processes utilizing zeolite microsieves can be classified into three groups:

(1) Hydrocarbon separation,
(2) Carbohydrate treatment, and
(3) Air separation.

Hydrocarbon separation is largely based on the production of linear paraffins from a variety of feed sources. The linear paraffin produced/extracted is used in synthetic detergent production, while the branched/cyclic isomer is produced as raffinate and is used to produce high octane gasoline and jet fuel.

Carbohydrate separations are generally limited to the food industry where fructose-glucose mixtures are separated in a two phase process. In the first phase, the fructose is separated as raffinate. In the second phase, the glucose containing saccharides are treated to adsorb glucose only. The selection of adsorbent is critical and zeolites compete with ion exchange resins.

Production of oxygen directly from small scale air separation systems are relatively common. Zeolites 5A and 13X are used to adsorb the nitrogen component.

The structural specifications for the most important zeolite adsorbents are listed below:

STRUCTURAL SPECIFICATIONS FOR ZEOLITE A

PARAMETER	**ZEOLITE**		
	3A	**4A**	**5A**
Unit Cell Contents	$K_{12}(A\text{-}S)_{12}$	$Na_{12}(A\text{-}S)_{12}$	$Ca_6(A\text{-}S)_{12}$
Dimensions (Angstroms)	-	12.3-(Cubic)	-
Si/Al Ratio	-	0.9 to 1.0	-

3.2.4.2 Zeolite Specifications (Cont'd)

STRUCTURAL SPECIFICATIONS FOR ZEOLITE A (Cont'd)

PARAMETER	**ZEOLITE**		
	3A	**4A**	**5A**
Framework Density (g/cm^3)	-	1.27	-
Crystal Density (g/cm^3)	1.69	1.52	1.48
Pore Diameter (Angstroms)	3.0	3.8	4.3
Largest Molecules	H_2O	C_2H_6	CF_4, n- paraffins

NOTE: A = AlO_2 and S = SiO_2

3.2.4.2 Zeolite Specifications (Cont'd)

STRUCTURAL SPECIFICATIONS FOR ZEOLITES X, Y AND ZSM-5

PARAMETER	FAUJASITE		SILICALITE
	ZEOLITE X	ZEOLITE Y	ZSM-5
Unit Cell Contents	$Na_{86}(A_{86}\text{-}S_{106})$	$Na_{56}(A_{54}\text{-}S_{136})$	S Na_nS_{96} A_{96-n}
Dimensions (Angstroms)	Cubic, 12.5	Cubic, 12.35	Rhombic, 20.1,19.9,13.4
Si/Al Ratio	1.0 to 1.5	-	-
Framework Density (g/cm^3)	1.31	1.25 to 1.29	1.76
Crystal Density (g/cm^3)	1.54	1.42	
Pore Diameter (Angstroms)	8.1+	8.1	
Largest Molecules	$(C_4F_9)_3N$, dimethyl naphthalenes	-	CCl_4, m-xylene

NOTE: A = AlO_2 and S = SiO_2

3.2.4.2 Zeolite Specifications (Cont'd)

The general specifications for Linde molecular sieves are summarized below. Further details are contained in Appendix II.

LINDE MOLECULAR SIEVE SPECIFICATIONS

PARAMETER			VALUE
Pore Size (Angstroms)	-	3A	3
	-	4A	4
	-	5A	5
	-	13X	10
Heat of Adsorption			1.16 kWh/kg
External Surface Area			1 to 3 m^2/g
Internal Surface Area			700 to 800 m^2/g
Macro Void Volume			0.28 to 0.35 cm^3/g
Specific Heat			0.25 cal/g/C

3.2.4.3 Market Trends

Microsieve grade zeolites used in adsorbent and desiccant applications consume approximately 10% of the total zeolite production. The market has been growing at around 5% per annum and is predicted to so do through the early 1990's. However, production has easily met the demand since a large majority of the catalyst producers are also associated with microsieve applications.

3.2.4.3 Market Trends (Cont'd)

Although synthetic zeolite producers argue that it is impossible to control product purity and hence the properties of natural zeolites, it is often the natural minerals that are used as the feedstock to synthetic zeolite processing. Microsieve manufacturers tend to follow this practice, especially in the area of specialized processing where precise control of the final zeolite product is of crucial importance to the process to which the zeolite will be applied.

3.2.5 Filler Application

The use of zeolites in filler/extender applications is very limited. Normal filler applications include the following areas:

(1) Plastics

(2) Cements, and

(3) Papers.

3.2.5.1 Plastics

There are no applications using zeolites as plastic fillers. Although the intrinsic physical properties of zeolites enable them to bind well with the plastic, there appears to be no cost advantage over present fillers on the market. The present fillers include: calcium carbonate, kaolin and other natural stone extenders.

3.2.5.1 Plastic (Cont'd)

The application for zeolites, according to the patents presently being listed, would likely be in areas where their unique properties are utilized as "value added" materials. An area in which some interest has been shown is in the production of solid polyurethane foams. During the reaction between isocyanate and polyol, the water that is present reacts with isocyanate to liberate carbon dioxide. This blowing action is highly desirable in the production of foams, but not when a homogeneous solid is desired. The addition of a suitable zeolite in the formulation causes uptake of the water to the zeolite during the initial polymerization, with the result that secondary CO_2 production is inhibited. Indeed the zeolite may adsorb any other low molecular mass compound which might be deleterious to the desired product. As yet, this application has been proven with only "pure" zeolite additions and is limited to a single process.

A second example of a plastic filler application is in the production of high mineral phase sheets. The surface of the sheet is treated with zeolite mineral or with other mineral fillers in order to improve the final properties of the fibre sheet. Again no production details are available and the application extremely limited.

The use of "loaded" zeolites has been proposed as an application in the production of solid air deodorants. Porous zeolite is treated with a deodorant molecule. The zeolite is then bound in a "porous" plastic case and the deodorant then decays to the atmosphere with time.

A similar technique has been proposed in conjunction with the hardening of dental fillings. Zeolites could be used as carriers for hardening catalysts in dental formulations based either on metal or organic matrices. The release of the catalyst over a short period of time allows hardening of the filling matrix after a suitable moulding time.

It is clear that bulk filler applications using zeolite in plastics have yet to be formulated. An appraisal of the literature tends to reveal that any future applications will likely involve pure synthetic zeolites or high purity natural zeolite forms. If markets are developed, it appears that they will be novel low volume applications.

3.2.5.2 Cements

The application of zeolite as cement filler is generally conceded to be relatively limited at the present time. The application of flyash in concrete, however, is well documented, particularly in the field of alkali aggregate reactivity suppression. Excess metal alkalis are preferentially combined before reacting with silicate bearing aggregate. It would appear likely that zeolite flyash may provide some interest in this area.

One area of application receiving considerable interest is the production of high early strength concrete utilizing limestone and zeolite as fine powder. Though the zeolite essentially behaves as ground slag or flyash in promoting long term strength, it particularly provides high sulfate resistance and low heat of hydration during curing. These advantages must be balanced against the high water requirements usually present in zeolite cement and the ensuing low early strengths usually observed during curing.

The performance of a particular zeolite depends greatly on the individual properties of that zeolite. In countries where pozzolan additions to cement formulae are highly desirable, i.e. where clinker production costs are to be minimized, the use of zeolite in cement formation is common, e.g. China, Russia, etc. Natural zeolites commonly used are usually mordenite or clinoptilolite. In North America zeolite utilization is limited but not unknown. The formulation, type of zeolite and application is usually proprietary and detailed information difficult to acquire.

3.2.5.3 Papers

In areas where natural paper fillers are not prevalent, attempts have been made to incorporate natural zeolites as paper fillers. Notably, in Japan the Zeiklite manufacturing company utilizes a bleached clinoptilolite (natural zeolite) in paper manufacturing. The company produces some 50,000 to 60,000 tpa of the white zeolite exclusively for the paper industry.

Clearly any application in the pulp and paper industry requires that the zeolite compete with more traditional fillers, such as kaolin, both in price and in quality. Due to the plentiful kaolin resources in the North American market this application has not been investigated seriously.

3.2.5.4 Plastic Filler Specification

The specification for fillers that are currently used by the plastics industry is given below:

SPECIFICATIONS FOR PLASTIC FILLERS

PROPERTY	PLASTIC FILLER		
	CALCIUM CARBONATE	TALC	GLASS SPHERES
Specific Gravity (1)	2.71	2.85	2.48
Bulk Density (g/cm^3)	1.15	-	-
Packing Factor (%)	42.4	-	-
Particle Size (microns) (2):			
Mean	3.5	7.6	31.7
Median	3.6	8.8	33.6
Surface Area (m^2/g) (3)	3.26	17.50	0.10
Hegman Finess (4)	6	4	3
Oil of Adsorption (5)	21.5	29	17.5
pH (6)	9.2 to 9.7	9.5	9.5
Dry Brightness (%) (7)	94	89	61

NOTES:
(1) Air Pychometer, ASTM D2840
(2) Coulter Counter
(3) BET (Nitrogen)
(4) ASTM D1210
(5) ASTM D281
(6) ASTM D3100
(7) ASTM E97

3.2.5.4 Plastic Filler Specification (Cont'd)

For the sake of comparison, the effect of the above fillers on the mechanical properties of polypropylene is shown below:

MECHANICAL PROPERTIES OF FILLED POLYPROPYLENE

FILLER	FILLER LOADING (% w/w)	IZOD IMPACT (ft-lb/in)	FLEXURAL MODULUS (psi x 10^{-3})	YIELD STRENGTH (psi x 10^{-3})	ELONGATION (AT BREAK) (%)
No Filler	0	1.3	135	3.4	93
Calcium	20	0.9	192	2.9	33
Carbonate	30	0.8	228	2.7	23
Grade I	40	0.7	281	2.7	12
Talc	20	0.8	247	3.3	15
	30	0.6	325	3.2	11
	40	0.5	379	3.2	8
Glass	20	0.8	167	2.7	19
Spheres	30	0.6	182	2.4	48
	40	0.6	217	2.1	43

The above results show that the fillers in general caused a drop in the value for Izod impact strength. The drop in impact strength increased with the amount of filler used.

3.2.5.4 Plastic Filler Specification (Cont'd)

On the other hand, the fillers all resulted in an increase in flexural modulus of the polypropylene. The increase in flexural modulus was largest when talc was used as the filler. With a filler loading of 40% talc, the flexural modulus was increased by almost a factor of 3 over the unfilled polypropylene.

The results indicated that the filler has only a minor effect on the yield strength. When talc was used as the filler, the effect on yield strength was insignificant.

The general effect of the filler was a sharp reduction in the ability of the plastic to deform and stretch. Thus, elongation of polypropylene at the break point was sharply reduced when the fillers were added, with the largest reduction recorded for talc. The results for the glass spheres were different from those of talc and calcium carbonate. Unlike the powders, the decrease in polypropylene elongation was less when a higher loading of glass spheres was used. In any case, the effect of the fillers was to provide a stiffer but more brittle product.

3.2.6 New Technology and Trends for Zeolites

3.2.6.1 New Technology

With 1000 patent applications per annum associated with zeolite technology, the development of both unique processes and new zeolite hybrids is overwhelming.

Within the petrochemical industry, continued development of the ZSM-5 catalyst, particularly for FCC catalysts, is prevalent. The major interest appears to be in extending substitutions of elements such as Ga, Ge, B, Fe and Be into the framework in order to modify acid strength and improve catalytic properties. Recently discovered crystalline metal aluminophosphate zeolites have unique structures, including larger pore sizes than faujasite. In the meantime, faujasite itself is under constant study with the aim of improving the Si/Al ratio for more selective hydrocracking processes.

Distinguishing between zeolite catalysts and microsieve zeolites is becoming more difficult as innovations in both areas result in the creation of new zeolite materials that are suitable for both applications.

3.2.6.2 Flyash Treatment

In the synthesis of zeolites, further attention is now being paid to natural sources of zeolitic materials. Methods of activating or "regenerating" these materials are becoming prevalent. However, due to impurities, extreme limitations on natural zeolites are inevitable.

In Europe, some initial studies have been made on the direct conversion of flyash to consumable forms of zeolite. Specifically, the formation of faujasite and phillipsite has been documented. The proposed systems incorporate enclosed treatment of flyash with NaOH for long reaction times (40 days). The performance of these materials, particularly with regard to FCC applications has not been assessed. The production of zeolite A from flyash has also been attempted with some success using very short reaction times. In both of the above examples, complete transformation of the aluminosilicate phases in the flyash was not achieved. The best results were in the 50% conversion range. The Na/Al/Si ratios must be closely monitored for the correct transformation to take place. The projected uses for these new materials would be in "one-way" adsorption processes, i.e. where no regeneration is contemplated.

3.3 Properties of Unmodified Leach Residue

Four types of samples from the Carbovan process were analyzed by ORF (Appendix II), as follows:

SAMPLES ANALYZED BY ORF FOR PHYSICAL AND CHEMICAL CHARACTERISTICS

NO.	SAMPLE	DESCRIPTION
1	ESP/BH Float Tails	Tails from a decarbonizing flotation, whose feed was a 3:1 blend of ESP and BH flyash.
2	ESP/BH NaOH Leach Residue	Tails from leaching Sample 1 with sodium hydroxide at 200C for one hour. The dosage rate was 150kg sodium hydroxide/tonne ESP: BH flotation tails

3.3 Properties of Unmodified Leach Residues (Cont'd)

SAMPLES ANALYZED BY ORF FOR PHYSICAL AND CHEMICAL CHARACTERISTICS (Cont'd)

NO.	SAMPLE	DESCRIPTION
3	ESP/BH $NaOH/Na_2CO_3$ Leach Residue	Tails from leaching Sample 1 with sodium hydroxide and sodium carbonate at 200C for one hour. The dosage rates were 150kg sodium hydroxide/tonne ESP: BH flotation tails. 325 kg sodium carbonate/tonne ESP: BH flotation tails.
4	ESP $NaOH/Na_2CO_3$ Leach Residue	Tails from leaching ESP flotation tails with sodium hydroxide and sodium carbonate as in Sample 3.

NOTE: ESP = Electrostatic Precipitator Flyash
and BH = Boiler Hopper Flyash

The above samples were all thoroughly washed and oven dried at 110C prior to blending and sampling for analysis. Sample 1 was representative of the feed material originally planned for the Carbovan leaching process. (More recently, Carbovan has decided to start-up their Fort McMurray plant exclusively on ESP flyash). On the other hand, Samples 2, 3, and 4 should be typical of the unmodified leach residues leaving the Carbovan leaching process. Sample 4 was prepared specifically for characterization by x-ray diffraction methods.

The analytical/characterization results are presented in the following sections.

3.3.1 Physical Characterization

The physical characterization of the unmodified leach residue is summarized in the table below:

PHYSICAL CHARACTERISTICS OF UNMODIFIED LEACH RESIDUE

PROPERTY	SAMPLE	
	2	3
	ESP/BH NaOH LEACH RESIDUE	ESP/BH NaOH/Na_2CO_3 LEACH RESIDUE
Density (g/cc):	2.60	2.48
Wet	0.57	0.67
Tapped	0.59	0.79
Particle Size (microns):		
Image Analysis	14	13
Optical Analysis	15 ± 1.9	15 ± 1.9
Coulter Counter Analysis i)	9.5	i) 10.6
ii)	0.6	ii) 12.0
Surface Area (m^2/g) (1)	59.3	38.2
Pore Volume (cm^3/g) (1)	0.18	0.08
Average Pore Diameter (Angstroms)(1)	120.6	83.16
Oil Adsorption (2)	57.7	48.4
pH (3)	10.3	10.2

NOTES:
(1) Determined from BET measurements
(2) ASTM D281
(3) ASTM D3100

3.3.1 Physical Characterization (Cont'd)

The values for surface area, pore volume and pore diameter were determined by nitrogen BET measurements. Measurements were originally made by ORF (See Progress Reports 1 and 2 of Appendix II) but concerns existed with respect to the accuracy of the results. The samples were therefore sent to Micrometrics Instrument Corporation (Micrometrics) for surface measurements. The Micrometrics results are summarized in the above table and the data included in Progress Report 4 of Appendix II.

The average particle size was measured by three methods. Image and optical analyses appeared to give more consistent results, compared to Coulter Counter analysis. These two analyses indicated an average particle size of around 14 microns for the unmodified leach residue, independent of the leaching solution. This value agrees reasonably well with the 12 microns that was obtained from preliminary testing (Progress Report 1 of Appendix II).

However, when the value of 14 microns is compared to the 62 to 70 microns for FCC catalysts (Section 3.2.3.8), it must be concluded that the particle size of the unmodified leach residue is too fine. This probably explains the higher than usual pressure drop across the reactor observed during the preliminary tests by FCC MAT (Section 3.1).

On the other hand, a particle size of 14 microns is too large for detergent applications which call for a mean particle size that should be less than 4 microns, but never greater than 7.5 microns (Section 3.2.2.2). Thus, from a particle size point of view, the unmodified leach residue does not appear to be readily suited to the two major applications of zeolites; namely, as a detergent ingredient or as an FCC catalyst.

The particle size of the unmodified residue falls between those of talc (7.6 microns) and glass spheres (31.7 microns), (Section 3.2.5.4). Therefore, the size of the leach residue is acceptable for use as a plastic filler.

For microsieve applications, there are much more important properties to consider than particle size.

3.3.1 Physical Characterization (Cont'd)

Unlike particle size, surface area, pore volume and pore diameter all appear to be affected by the leaching operation. A mixture of sodium hydroxide and sodium carbonate yields a residue with less surface area, lower pore volume and smaller pore diameter.

FCC catalysts (Section 3.2.3.8) require large surface areas (between 300 and 400 m^2/g), high pore volume (between 0.4 and 0.9 cm^3/g) and small pore diameter (5 to 7.4 Angstroms). The small surface areas (38.2 and 59.3 m^2/g), low pore volume (0.08 and 0.18 cm^3/g), and large pore diameter (83.16 and 120.6 Angstroms) again indicated that the unmodified leach residues do not possess a suitable physical structure for use as FCC catalysts.

It should be noted that the large pore diameter reported for the residues is probably a reflection of the macro-porosity of the materials. Scanning electron microscopy work on the residue showed a high degree of fractured and porous ash particles. Thus, although the leach residue is zeolitic in nature, its molecular pore dimension was masked by the porous particle structure.

In any case, regardless of the porosity of the particles, the surface area of the residues is too low for application as FCC catalysts. The same argument should apply to detergent applications where a large surface area would be considered synonymous with a large exchange capacity. Similarly, in microsieve applications high surface areas in the order of 700 to 800 m^2/g (Section 3.2.4.2) are required.

From Section 3.2.5.4, it can be seen that the surface area requirements (0.10 m^2/g for glass spheres to 17.50 m^2/g for talc) for plastic fillers is quite low. The higher surface area for the leach residues (38.2 and 59.3 m^2/g) should therefore make them well suited for fillers. In addition, the porous nature of the particles should enhance bonding of the matrix to the particle surface. With regard to physical characteristics, the leach residue was well suited for filler applications.

3.3.2 Chemical Characterization

The results of chemical analysis of the flotation tails and unmodified leach residue are tabulated below:

CHEMICAL CHARACTERIZATION OF FLOTATION AND LEACH RESIDUES

COMPONENT	SAMPLE		
	1 ESP/BH FLOAT TAILS	2 ESP/BH NaOH LEACH RESIDUE	3 ESP/BH NaOH/ Na_2CO_3 LEACH RESIDUE
Oxides (%):			
SiO_2	49.69	44.26	42.48
Al_2O_3	24.57	22.38	22.60
Fe_2O_3	10.03	9.10	9.19
CaO	2.19	2.36	2.03
MgO	1.31	1.38	1.24
Na_2O	0.74	7.60	8.88
K_2O	1.67	0.95	0.28
TiO_2	3.40	3.08	3.10
MnO	0.20	0.19	0.18
P_2O_5	0.27	0.23	0.22
V	2.6	0.33	0.28

3.3.2 Chemical Characterization (Cont'd)

CHEMICAL CHARACTERIZATION OF FLOTATION AND LEACH RESIDUES (Cont'd)

COMPONENT	SAMPLE		
	1 ESP/BH FLOAT TAILS	2 ESP/BH NaOH LEACH RESIDUE	3 ESP/BH NaOH/ Na_2CO_3 LEACH RESIDUE
Cations (ppm):			
Ba	983	700	714
Sr	472	425	429
Zr	822	741	770
Be	5	5	5
Co	230	210	210
Cr	330	250	240
Cu	100	100	95
Pb	72	260	270
Ni	8,400	8,200	8,600
Cd	< 1	< 1	< 1
Ag	< 1	< 1	< 1
Mo	650	35	4
Zn	210	190	250
Sc	19	4	36
La	120	120	99
Ce	200	210	170
Nd	110	96	76

3.3.2 Chemical Characterization (Cont'd)

CHEMICAL CHARACTERIZATION OF FLOTATION AND LEACH RESIDUES (Cont'd)

COMPONENT	SAMPLE		
	1 ESP/BH FLOAT TAILS	2 ESP/BH NaOH LEACH RESIDUE	3 ESP/BH NaOH/ Na_2CO_3 LEACH RESIDUE
Sm	19	18	15
Eu	3.40	3.40	2.6
Tb	1.5	2.40	1.5
Yb	5.88	6.70	5.4
Lu	0.85	0.90	0.8
U	11.0	10.0	9.1
Th	38.0	34	26.0
Ga	-	10	10
Ge	-	43	28
Y	-	110	110
Other Components:			
Ammonium (ppm)	86	10.5	13.6
Nitrate as N (ppm)	< 0.1	< 0.1	2.8
Chlorine (ppm)	21	42	35
Sulphur (%)	0.11	0.060	0.13
Carbon (%)	0.60	1.00	1.30

3.3.2 Chemical Characterization (Cont'd)

Comparison of the chemical characteristics of FCC catalysts (Section 3.2.3.8) with those of the unmodified leach residues reveal a number of differences. Firstly, the carbon content of fresh FCC catalysts should be "zero". However, the flotation tails had a carbon content of 0.6%. What was even more surprising was the increase in carbon concentration of the zeolite during the leaching process to 1.00% for the NaOH leach residue and to 1.30% for the NaOH/Na_2CO_3 leach residue. These levels are much higher than the 0.20 to 0.25% found in the equilibrium catalyst. Therefore, lower catalytic activity from the fresh leach residue can be expected.

The second point to note is that, as expected, sodium is concentrated in the residue during the leaching process from 0.74% (as Na_20) for the flotation tails to 7.60 and 8.88% for the leach residues. These values are high compared to the 0.03 to 0.04% sodium in the FCC catalyst.

The third general characteristic of the leach residues was the high metals content. For example, the ferric oxide content in all cases was more than 9%, compared to 0.03 to 0.07% iron for the fresh FCC catalyst and 0.37 to 0.39% iron for the equilibrium catalyst (Section 3.2.3.8). In addition, the total concentration of vanadium, nickel and copper should be essentially zero for the fresh FCC catalyst, building up to less than 300 ppm for the equilibrium catalyst. In the case of the leach residues, the total concentration of these metals was more than 10,000 ppm.

Thus, from a chemical composition point of view, the leach residues again do not appear to provide the basis for a promising FCC catalyst.

The high metals content of the flotation tails and leach residues also precludes the use of these materials in detergent applications. The problem with the high metals content is even more serious since detergent grade zeolites can only tolerate a maximum dissolved metal ion content of 200 ppm. Moreover, the calcium and magnesium cations that cause water hardness are present in large amounts in the residues.

3.3.2 Chemical Characterization (Cont'd)

The high metals content would also affect the applicability of the leach residues as microsieves. For this application, the type and concentration of cation is tailored to provide the desired selectivity. In the case of the leach residues, the wide variety and high concentration of cations would only serve to make performance of the leach residues unreliable and unpredictable.

The high metals content could adversely affect the desirability of the leach residues for use as filler materials. This would be the case if the metals catalyze unwanted side reactions during the polymerization step. The metals might also lower the stability of the polymer itself.

As a last point, it should be noted that the metals content starts out high in the flotation tails. The subsequent leaching process selectively extracts only a few cations, such as vanadium, cobalt, chromium and molybdenum. But even the extraction of these metals is only partial. The rest of the metals remain on the leach residue thereby lowering its potential value in the above applications. These metals must first be removed and possibly recovered.

3.3.3 X-Ray Diffraction Characterization

Five samples were analyzed by XRD methods. There were 3 flotation tails and 2 leach residues, as follows:

SAMPLES ANALYZED BY XRD METHODS

NO	SAMPLE	COMMENTS
1	ESP/BH Float Tails	See Section 3.3
5	ESP Float Tails	Precursor to Sample 4
6	BH Float Tails	
2	ESP/BH NaOH Leach Residue	See Section 3.3.
4	ESP NaOH/Na_2CO_3 Leach Residue	See Section 3.3

3.3.3 X-Ray Diffraction Characterization (Cont'd)

Diffractometer traces were obtained on a Philips X-Ray Diffractometer, using a copper target tube that was powered by a Philips constant potential x-ray generator. Further details can be found in Appendix II.

3.3.3.1 Flotation Tails

The XRD results for the 3 flotation tails are summarized below:

XRD RESULTS FOR FLOTATION TAILS

SAMPLE	PHASES PRESENT (Wt %)				
	AMORPHOUS	QUARTZ	MULLITE	CALCITE	UNKNOWN
ESP/BH Float Tails	Major	15	5 to 10	1 to 2	5 to 10
ESP Float Tails	Major	6	2 to 5	-	5 to 10
BH Float Tails	Major	4	2 to 5	-	5 to 10

The bulk of all three samples was determined to be amorphous, with varying amounts of mullite ($Al_2O_3.SiO_2$), quartz (SiO_2), and in one case, calcite ($CaCO_3$). The 3 samples contained approximately the same amounts of unidentifiable material.

From the amorphous nature of the flotation tails, the characteristics of this material should resemble those of a clay to a greater extent than those of a zeolite.

3.3.3.2 Leach Residue

The XRD results for the 2 leach residues are tabulated below:

XRD RESULTS FOR LEACH RESIDUE

SAMPLES	PHASES PRESENT (Wt %)					
	ANALCIME	HARMOTOME	CALCITE	MULLITE	QUARTZ	UNKNOWN
ESP/BH NaOH Leach Residue	>50	10 to 20	-	2 to 5	1	5 to 10
ESP NaOH/ Na_2CO_3 Leach Residue	>50	-	2 to 5	1 to 2	1	5 to 10

Unlike the flotation tails, the major constituent in the leach residue was analcime, $Na(AlO_2.2SiO_2)H_2O$. This is the same major phase that was found in the leach residue from the preliminary tests (Section 3.1). However, there are differences in the amounts of the main phases that were identified in the two sets of leach residue. In the preliminary tests, more analcime was found in the NaOH/Na_2CO_3 leach residue than in the NaOH leach residue, while similar amounts were determined for the above two samples.

The NaOH leach residue contained some sodium harmotome, $Na(2AlO_2.6SiO_2)6H_2O$, while the other sample contained a minor amount of calcite.

Both samples contained similar amounts of unknown materials, quartz and mullite.

In general, it can be concluded that leaching is accompanied by the conversion of amorphous phase to analcime zeolite. This conversion means that the leach residue should behave more like a zeolite than a clay.

3.3.3.2 Leach Residue (Cont'd)

However, the structure of the analcime zeolite is different to that of the faujasite zeolites that are used in cracking, hydrocracking and molecular sieve applications. The form of the zeolite produced during the leaching process is therefore not immediately amenable to the above applications.

3.4 FCC Catalyst Testing

Six leach residue samples were sent to SRC for catalyst examination by the FCC MAT procedure. This was the same procedure used in the preliminary testing performed in 1986 (Section 3.1 and Appendix I). The 6 residue samples are listed below:

SAMPLES EVALUATED BY FCC MAT PROCEDURE

NO.	SAMPLE	DESCRIPTION
1	ESP/BH Float Tails	See Section 3.3
2	ESP/BH NaOH Leach Residue	See Section 3.3
3	ESP/BH NaOH/Na_2CO_3 Leach Residue	See Section 3.3
4	ESP NaOH/Na_2 CO_3 Leach Residue	See Section 3.3

3.4 FCC Catalyst Testing (Cont'd)

SAMPLES EVALUATED BY FCC MAT PROCEDURE (Cont'd)

NO.	SAMPLE	DESCRIPTION
7	Sample 4 + 20% Al_2O_3	Sample 4 mixed with 20% Al_2O_3
8	ESP NaOH Leach Residue	Tails from a decarbonizing flotation, whose feed was ESP flyash. This flotation tail was leached with sodium hydroxide as in Sample 2.

NOTE: ESP = Electrostatic Precipitator and BH = Boiler Hopper

3.4.1 FCC-MAT Results

The results of the FCC-MAT evaluations that were performed by SRC (Appendix III) are tabulated below. For the sake of comparison, the results from the preliminary tests (Section 3.1) are included.

FCC-MAT RESULTS

TEST	LEACH RESIDUE			SAND				
NO.	SAMPLE	WT (g)	TREATMENT	WT (g)	TREATMENT	REACTON TEMP (^0C)	CONV-ERSION TO GASOLINE (WT %)	GAS (ML)
1	1P	3	Decoke (120-590C,5h)	-	-	482	43.4	40
2	2P	4	Dry (120-150C, o/night)	-	-	504	41.1	97
3	2P	4	Dry (350C, 1.5h extra)	-	-	504	47.7	109
4	2P	3	Dry (350C, 1.5h)	1.5	Decoke (650C,5h)	504	61.0	62
5	3P	4	-	-	-	482	40.0	64
6	2(ESP/BH NaOH)	3	-	-	-	482	21.1	30
7	2(ESP/BH NaOH)	3	Decoke (450C, 3h)	1.5	Decoke (450C,3h)	482	26.9	29
8	3(ESP/BH NaOH/ Na_2CO_3)	3	Decoke (450C, 3h)	1.5	Decoke (450C,3h)	483	21.4	30
9	1(ESP/BH)	4	Decoke (450C, 3h)	1.5	Decoke (450C,3h)	482	25.5	6
10	4(ESP NaOH/ Na_2CO_3)	4	-	-	-	482	27.6	50
11	4(ESP NaOH/ Na_2CO_3)	3	Decoke (450, 3h)	1.5	Decoke (450C,3h)	482	28.0	38.5
12	7(4+20% Al_2O_3)	4	-	-	-	482	31.6	54.5
13	7(4+20% Al_2O_3)	3	Decoke (450C, 3h)	1.5	Decoke (450C,3h)	482	25.2	50.0
14	8(ESP NaOH)	4	-	-	-	482	29.4	38.5
15	8(ESP NaOH)	3	Decoke (450C, 3h)	1.5	Decoke (450C,3h)	482	28.1	39.5

FCC-MAT RESULTS (Cont'd)

TEST	LEACH RESIDUE			SAND				
NO.	SAMPLE	WT (g)	TREATMENT	WT (g)	TREATMENT	REACTON TEMP (^oC)	CONV-ERSION TO GASOLINE (WT %)	GAS (ML)
16	2P	3	Decoke (450C, 3h)	1.5	Decoke (650C, 5h)	504	33.8	42.0
17	7(4 + 20% Al_2O_3)	4	-	-	-	504	35.7	72.0
18	2P	4	Dry (350C, 1.5h)	1.5	-	504	33.5	30.0
19	2P	4	Decoke (350C, 6H)	-	-	504	32.9	32.0
20	Sand	-	-	8	Decoke (650C, 5h)	504	8.6	18.0
21	3P	4	Dry (120C,20h)	-	-	504	38.5	90.5
22	Comm. Equil.	4	Decoke (120-590C, 5h)	-	-	482	65.4	-
23	Comm. Equil.	4	Decoke (120-590C, 5h)	-	-	504	72.3	-

3.4.1 FCC MAT Results (Cont'd)

The FCC MAT results have been divided into the following 4 groups:

GROUPINGS OF FCC MAT RESULTS

GROUP	TESTS	DESCRIPTION
1	1 to 5	Preliminary test results (See Section 3.1)
2	6 to 15	Testing of float tails and leach residues listed in Section 3.4
3	16 to 21	Repeat runs, plus sand reference
4	22 and 23	Commercial FCC catalyst

Group 1 contains the results for 5 of the 6 runs conducted during preliminary testing. Test 4 of this group was done with a synthetic gas oil feed, while all other tests in the above table were done with conventional feeds. It should again be noted that this test (Test 4) gave the highest conversion (61%) of gas oil to gasoline, and was the major factor that led to the preparation of a proposal for this project. Other tests with the three leach residues gave average conversion rates of 42% at 482C and 44% at 504C. Thus, the preliminary tests indicated that, by simply adding sand to improve diffusion characteristics, the catalytic activity of the leach residue could be substantially improved to increase the gas oil-to-gasoline conversion rate from 44% to 61%. The conversion rate of 61% was comparable to clay catalysts but still slightly lower than commercial zeolite catalysts.

The aim of the current tests therefore, was to improve the conversion rate of the leach residues to levels that would be comparable to commercial zeolite catalysts. Conversion rates of 75 to 85% was considered ideal for FCC catalyst applications. All tests in Groups 2, 3 and 4 were done with the same conventional gas oil feed.

3.4.1 FCC-MAT Results (Cont'd)

The first two tests in Group 2 (Tests 6 and 7) were conducted with a caustic leach residue. The results showed that the conversion rate was increased by 6% from 21% to 27% due to the combined treatment of decoking the residue and mixing it with sand. However, the conversion rate was disappointingly low.

Another leach residue was tested. This time the residue was obtained from leaching with caustic and sodium carbonate (Test 8). A low conversion rate of 21.4% was again obtained.

The fourth test of Group 2 (Test 9) was carried out with a flotation tails. A conversion rate of 25.5% was obtained, indicating no improvement in activity of the leach residue over the flotation tails. This result was unexpected since XRD analysis (Section 3.3.3.1) showed the main phase of the flotation tails to be amorphous, while the major phase in the leach residue was analcime. Greater catalytic activity for the leach residue was therefore expected since leaching was accompanied by the conversion of the amorphous phase to a crystalline zeolite phase.

Tests 10 and 11 were carried out with another caustic/carbonate leach residue. This time the conversion rates of 27.6 and 28.0% indicated that decoking of the residue and mixing with sand had no effect on catalytic activity. This result contrasts with the improvement shown in test 6 over test 7.

This trend was also evident in the next four tests (Tests 12 to 15). For Tests 12 and 13, Residue 4 was mixed with 20% alumina. Conversion rates of 31.6% and 25.2% were obtained, with the lower conversion rate for the decoked and sand-mixed residue. This result again contrasts to that found for Tests 6 and 7. Similarly, the decoked and sand-mixed residue in Test 15 gave a slightly lower conversion rate (28.1%) than in Test 14 (29.4%).

In summary, for Group 2 the best conversion rate was obtained with Sample 7. An average conversion rate of 27.4% was obtained for the untreated leach residues, and 27.1% for the corresponding residues that were decoked and mixed with sand.

3.4.1 FCC-MAT Results (Cont'd)

These virtually identical results indicated that no increase in catalytic activity was achieved by decoking and mixing with sand. Moreover, these conversion rates are only marginally better than the 25.5% obtained for the flotation tails.

In addition, the average combined conversion rate of 27.2% obtained at 482C was only 65% of the rate (42%) for the preliminary tests at the same temperature. The tests in Group 3 were performed in an attempt to explain the cause of the discrepancies between the Group 1 and Group 2 results.

3.4.2 Discrepancy Between Preliminary and Current Tests

The main factors that could affect the conversion rate are:

(1) The gas oil feed,
(2) The leach residue, and
(3) The FCC MAT equipment.

The first test (Test 16) in Group 3 was meant to be a duplicate of Test 4 (Section 3.4.1). However, the decoking of the leach residue was carried out at a higher temperature (450C) and longer time (3 hours) in Test 16 that in Test 4 (350C and 1.5 hours). In view of the Group 2 results, the coking procedure was not expected to have a significant bearing on the results. Therefore, the difference in conversion rate between Test 16 (33.8%) and Test 4 (61.0%)must be explained in terms of the feed and equipment. Indeed, Test 4 was the only one conducted with a synthetic gas oil feed. The effect of the feed on catalytic performance should therefore be further investigated in order to fully resolve this difference in results. (A summary of the characterisation of both synthetic and conventional gas oils is included in Appendix IV.)

Test 17 was supposed to be a duplicate of Test 12. However, the reaction temperature for Test 17 was 504C, while it was 482C for Test 12. In order to compare the results on the same basis, the effect of temperature on conversion rate was estimated using Tests 22 and 23. Both tests were conducted under identical conditions except for temperature. The ratio of the conversion rates at 482C and 504C was calculated to be 65.4/72.3 = 0.905. By multiplying the conversion rate for Test 17 by this factor, an estimate of the rate at 482C can be obtained. The rate at 482C was estimated to be 32.3%, compared to 31.6% for Test 12. This appears to indicate that good reproducibility can be achieved using the FCC MAT equipment.

3.4.2 Discrepancy Between Preliminary and Current Tests (Cont'd)

Tests 18 and 19, with conversion rates of 33.5 and 32.9% respectively, confirm that the addition of sand has very little beneficial effect on the formation of gasoline, although it might be useful in lowering the pressure drop across the reactor.

The average conversion rate for Sample 2P during preliminary testing at 504C was: (41.1 + 47.7)/2 = 44.4% (excluding Test 4 with the synthetic gas oil). The corresponding average conversion rate for the repeat runs was: (33.8 + 33.5 + 32.9)/3 = 33.4%. The ratio of the two average conversion rates is: 33.4/44.4 = 0.75. Thus, since the same leach residue was used, and assuming good experimental reproducibility, the results of the repeat tests (Group 3) indicate that the conversion rate was only 75% of the rate obtained from the preliminary tests. The reason for the lower conversion rate of the Group 2 and 3 tests can only be explained by differences in the feed material.

As mentioned above, this would also explain the high conversion rate observed for Test 4 when the synthetic gas oil was used. It would appear that the leach residue is very sensitive to the feed material. In such a case, impurities in the gas oil could significantly affect catalyst performance.

If the Group 2 test results are converted to 504C results (by dividing by the 0.905 factor) and to the gas oil feed used in the preliminary tests (by dividing by the factor 0.75), then the Group 2 test results could be compared directly to the Group 1 preliminary test results. This is shown below:

CONVERSION OF TEST RESULTS TO 504C AND PRELIMINARY FEED

TEST NO	I CONVERSION RATE AT 482C (%)	II CONVERSION RATE AT 504C (I/0.905) (%)	III CONVERSION RATE AT 504C + PRELIM FEED (II/0.75) (%)
6	21.1	23.3	31.1
7	26.9	29.7	39.6
8	21.4	23.6	31.5
9	25.5	28.2	37.6
10	27.6	30.5	40.7

3.4.2 Discrepancy Between Preliminary and Current Tests (Cont'd)

CONVERSION OF TEST RESULTS TO 504C AND PRELIMINARY FEED (Cont'd)

TEST NO	I CONVERSION RATE AT 482C (%)	II CONVERSION RATE AT 504C (I/0.905) (%)	III CONVERSION RATE AT 504C + PRELIM FEED (II/0.75) (%)
11	28.0	30.9	41.2
12	31.6	34.9	46.5
13	25.2	27.8	37.1
14	29.4	32.5	43.3
15	28.1	31.0	41.3

Examination of Column III reveals that the converted Group 2 results are comparable to those obtained during the preliminary tests. Of the Group 2 tests, the best conversion rate was obtained with Test 12, using the mixture of Sample 4 and alumina.

3.4.3 Comparison of Catalyst Properties

Comparison of the properties of Sample 3 (ESP/BH NaOH/Na_2CO_3 Leach Residue) with those of a commercial FCC catalyst and a pillared clay (bentonite) clay is shown below:

3.4.3 Comparison of Catalyst Properties (Cont'd)

COMPARISON OF LEACH RESIDUE WITH COMMERCIAL FCC CATALYSTS

PROPERTY	FCC CATALYST (FRESH HEZ-55)	BENTONITE CLAY (PILLARED)	LEACH RESIDUE (SAMPLE 3)
Chemical Analysis:			
Al_2O_3 (Wt %)	58.0	26.2	22.6
$Si O_2$ (Wt %)	36.0	54.5	42.5
$Ti O_2$ (Wt %)	2.4	-	3.1
Na_2O (Wt %)	0.6	0.4	8.9
Fe_2O_3 (Wt %)	0.6	4.6	9.2
CaO (Wt %)	-	0.2	2.0
MgO (Wt %)	-	2.4	1.2
K_2O (Wt%)	-	0.8	0.3
V (ppm)	< 150	-	2800
Ni (ppm)	< 150	-	8600
Zeolite (Wt %)	20.0	-	-
Physical Analysis:			
Surface Area (m^2/g)	288	270	38.2
Pore Volume (ml/g)	0.4	0.2	0.1
Bulk Density (g/ml)	0.9	-	0.7
Avg. Particle Size (microns)	70.0	-	15.0

3.4.3 Comparison of Catalyst Properties (Cont'd)

Compared to the FCC catalyst, both the pillared clay and leach residue were short on alumina. It was therefore not surprising that the addition of 20% alumina was accompanied by an increase in catalytic activity - refer to Tests 10 and 12 in Sections 3.4.1 and 3.4.2.

However, even with the added alumina, the activity of the leach residue was slightly less than half that of the commercial FCC catalyst. This can be seen by comparing the conversion rates for Tests 12 and 22 in Section 3.4.1.

The catalytic activity of the sand alone (Test 20 in Section 3.4.1) was determined along with the repeat tests. Comparison of this result with Test 17 showed that, even though the weight of sand used was twice that of the leach residue, the residue was still more than 4 times as active as the sand. Thus, it can be concluded that the leach residue possesses significant catalytic activity, although it is only half that of a commercial FCC catalyst.

As mentioned before (Section 3.3.2), the metals content of the leach residue is extremely high. The high metals content at least partially explains the lower activity of the leach residue, as well at its sensitivity to the type of gas oil feed. Thus, a synthetic gas oil with a very low impurities content should provide higher conversion rates than a conventional gas oil feed. Reduction of the metals content in the leach residue would therefore be highly desirable.

Also desirable would be improvement in the physical properties of the residue, especially surface area, pore volume and particle size (Section 3.3.1).

The data collected from the project thus far, all point to the shortcomings of the leach residue as an FCC catalyst. It is believed that major changes to the leach residue must be made before the activity and durability of the material could approach those of a commercial FCC catalyst. Such changes, while possible, could be very costly. Knowing that the zeolite market is competitive and saturated, the cost of such changes should be carefully evaluated to determine if the product would satisfy the criteria of being a "low cost" catalyst.

3.4.3 Comparison of Catalyst Properties (Cont'd)

For this reason, the experimental work was prematurely terminated in order to carefully assess the situation. This was believed to be preferable to plunging blindly onward.

3.4.4 Future Work

There is no doubt that the leach residue must be improved before it can compete with commercial catalysts. However, the cost of the improvement must be carefully considered if the resultant catalyst is to be economically competitive. A systematic study to identify an effective and economical method of improving the properties of the leach residue must be done before any further experimental work is performed. Such a study will benefit greatly from the information collected in this project.

The study must cover two main areas:

(1)	Chemical Properties	- the alumina/silica ratio should be improved to FCC catalyst levels;
		- the metals content should be reduced to acceptable levels for an active and durable catalyst;
(2)	Physical Properties	- the major phase should be converted to a crystalline form that is compatible with the faujasite structure in order to provide acceptable pore dimensions;
		- the surface area should be greatly increased to at least $300m^2/g$. One method might be interlaying the leach residue with a polymer such as aluminum chlorhydroxide.

The Carbovan process must be carefully reviewed to determine if the required changes could be incorporated into the leaching process without substantially affecting product yield and cost.

3.5 Evaluation of Alternate Leach Residue Uses

For the evaluation, a large batch sample of NaOH leach residue was prepared. The residue was thoroughly blended prior to sampling and testing for use in four potential areas. A representative portion of the leach residue (Sample 2 in Section 3.3) was also assayed and the basic physical properties assessed (Sample 2 in Section 3.3.1).

The four potential areas for application of the leach residue that were tested are as follows:

(1)	FCC Catalyst	- 250g Sample tested by SRC - Section 3.4
(2)	Detergent	- 100g Sample tested by ORF - Section 3.5.1
(3)	Microsieve	- 250g Sample tested by Nova Husky - Section 3.5.2
(4)	Plastic Filler	- 2kg Sample tested by ORF - Section 3.5.3.

The data for these tests are included in Appendix II and III, and the results discussed in the sections as indicated above.

3.5.1 Detergent Testing

Standard test procedures for zeolites in detergent formulations are commonly found in the literature. The tests are initially based on determining the uptake of dissolved calcium and magnesium from standard water solutions. Providing the zeolite complies with this basic test and meets all other specifications, detergent formulations, and ultimately the cleaning performance of the final detergent, can be monitored.

The basic test procedure consists of formulating a standard tap water of known Ca^{++} and Mg^{++} ion concentration. The concentrations of Ca^{++} and Mg^{++} should approach those expected in the area of use. Two standard solutions were tested. Solution A with 40 mg Ca/l and 8.4 mg Mg/l, and solution B with 16.0 mg Ca/l and 5.2 mg Mg/l.

3.5.1 Detergent Testing (Cont'd)

The decrease in water hardness was measured as a function of zeolite contact time, the temperature during contact and the concentration of zeolite present. Washing conditions were simulated by carrying out determinations at room temperature. Solids concentrations varied from 0.03g to 0.09g per 100 mls. solution. Aliquotes of the solution were taken at 1 minute, 5 minute and 10 minute intervals after the initial slurrying. The samples were filtered and the filtrate analyzed by atomic absorption spectroscopy for Ca and Mg ion concentration.

The tests were repeated for both the material under test as well as for a standard commercial zeolite A used in detergent formulations. The zeolite material tested was a caustic leach residue from a 3:1 ESP/BHA feed (Sample 2 in Section 3.3), while the standard was Ethyl zeolite A manufactured by Ethyl Corporation, U.S.A.

The leach residue under test was then reported as having a maximum equivalent calcium ion capacity, which is reported as mg Ca^{++}/gram residue.

The results for Solution A are tabulated below:

COMPARISON OF LEACH RESIDUE WITH ZEOLITE A USING SOLUTION A

ZEOLITE	AMOUNT OF SORBENT (g/100ml Soln. A)	CONTACT TIME (min)	Ca^{++} ION CONTENT (ppm)	Mg^{++} ION CONTENT (ppm)	ION UPTAKE Ca (mg/g)	ION UPTAKE Mg (mg/g)
Leach Residue	0.03	0	16	5.2	0.0	0.0
		1	17	5.3	-3.3	-0.3
		5	17	5.3	-3.3	-0.3
		10	17	5.3	-3.3	-0.3
	0.06	1	17	5.1	-1.7	0.2
		5	16	5.0	0.0	0.3
		10	17	5.1	-1.7	0.2
	0.09	1	16	4.9	0.0	0.3
		5	16	4.8	0.0	0.4
		10	17	4.9	-1.1	0.3

3.5.1 Detergent Testing (Cont'd)

COMPARISON OF LEACH RESIDUE WITH ZEOLITE A USING SOLUTION A (Cont'd)

ZEOLITE	AMOUNT OF SORBENT (g/100ml Soln. A)	CONTACT TIME (min)	Ca^{++} ION CONTENT (ppm)	Mg^{++} ION CONTENT (ppm)	ION UPTAKE Ca (mg/g)	Mg (mg/g)
Zeolite A	0.03	0	16	5.2	0.0	0.0
		1	8.4	5.1	35.3	0.3
		5	3.2	5	42.6	0.6
		10	0.9	4.8	50.0	1.3
	0.06	1	1.1	4.6	24.8	1.3
		5	0.1	4.8	26.5	0.6
		10	0.1	4.5	26.5	1.2
	0.09	1	0.1	4.5	17.6	0.8
		5	0.3	3.4	17.4	2.0
		10	0.1	3.5	17.6	1.9

3.5.1 Detergent Testing (Cont'd)

The corresponding results for solution B are as follows:

COMPARISON OF LEACH RESIDUE WITH ZEOLITE A USING SOLUTION B

ZEOLITE	AMOUNT OF SORBENT (g/100ml Soln. B)	CONTACT TIME (min)	Ca^{++} ION CONTENT (ppm)	Mg^{++} ION CONTENT (ppm)	ION UPTAKE Ca (mg/g)	ION UPTAKE Mg (mg/g)
Leach Residue						
	0.03	0	40	8.4	0.0	0.0
		1	38	8.1	6.7	1.0
		5	40	8.3	0.0	0.3
		10	37	8.1	10.0	1.0
	0.06	1	38	8.1	3.3	0.5
		5	34	8.3	10.0	0.2
		10	38	8.2	3.3	0.3
	0.09	1	38	8.1	2.2	0.3
		5	40	8.1	0.0	0.3
		10	39	7.9	1.1	0.6

3.5.1 Detergent Testing (Cont'd)

COMPARISON OF LEACH RESIDUE WITH ZEOLITE A USING SOLUTION B (Cont'd)

ZEOLITE	AMOUNT OF SORBENT (g/100ml Soln. A)	CONTACT TIME (min)	Ca^{++} ION CONTENT (ppm)	Mg^{++} ION CONTENT (ppm)	ION UPTAKE Ca (mg/g)	ION UPTAKE Mg (mg/g)
Zeolite A						
	0.03	0	40	8.4	0.0	0.0
		1	27	8.3	43.3	0.3
		5	22	8.4	60.0	0.0
		10	19	8.2	70.0	0.7
	0.06	1	16	8.1	40.0	0.5
		5	6.1	8.4	56.5	0.0
		10	2.4	8.2	62.7	0.3
	0.09	1	11	8.4	32.2	0.0
		5	1	7.5	43.3	1.0
		10	1.5	6.4	42.8	2.2

At the lower ion concentration (Solution A), ion uptake by the leach residue was almost non existent. In fact, there appeared to be a slight release of ions to Solution A rather than an uptake. This result was not surprising in view of the high levels of calcium and magnesium in the leach residue (Section 3.3.2).

3.5.1 Detergent Testing (Cont'd)

On the other hand, the commercial zeolite A was able to reduce the calcium ion concentration in Solution A to the 0.1 ppm level. The maximum calcium ion uptake that was observed with Solution A was 50 mg/g zeolite. It should be noted that the adsorption of ions on the zeolite is time dependent. Therefore, contact times should be long enough to establish equilibrium concentrations in order to obtain the maximum ion uptake.

It should also be noted that the adsorption capacity of zeolite A for magnesium was poor. This is explained by the large ionic radius of magnesium compared to the pore openings of zeolite A (Section 3.2.2.2).

At the higher ion concentration (Solution B), the leach residue showed slight uptakes of both calcium and magnesium. However, the maximum adsorption capacity of 10 mg Ca/g for the leach residue was still on the low side compared to 70mg Ca/g for zeolite A.

The uptake of magnesium by zeolite A was again moderate and only marginally better than the leach residue.

The general conclusion that can be drawn from the above results is that the leach residue performed poorly against zeolite A with regard to calcium ion uptake. The leach residue therefore failed the basic test. Thus, further testing of the leach residue for detergent applications was not carried out.

3.5.2 Microsieve Testing

Nova Husky Research Corporation (NHRC) was contracted by ORF to evaluate the molecular sieve capabilities of the leach residue (Sample 2 in Section 3.3.). This was to be accomplished by comparing the capacity of the leach residue to adsorb moisture against that of a commercial zeolite. Because of the large pore diameter of the leach residue (Section 3.3.1), the Union Carbide 13X zeolite with a pore size of 10 Angstroms was selected as the commercial reference zeolite. Comparison of the two materials is shown below:

3.5.2 Microsieve Testing (Cont'd)

COMPARISON OF LEACH RESIDUE WITH ZEOLITE 13X

PROPERTY	ESP/BH NaOH LEACH RESIDUE	UNION CARBIDE ZEOLITE 13X
Surface Area (m^2/g)	59	300
Pore Diameter (Angstroms)	121	10
Bulk Density (Tapped) (g/cm^3)	0.59	0.51
Initial H_2O Content (Wt%)	5.7	2.5
Equilibrium H_2O Capacity (Wt%)	To Be Determined	26

3.5.2.1 Experimental Procedure

Initial assessment of the moisture capacity of the leach residue zeolite material was performed using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The GC was configured in such a way as to minimize the distance from the injector port to the zeolite column and the distance of the zeolite column to the detector. A small length of 1/16" 316SS tubing was used to connect the exit of the injector port to the bottom of a 1/8" x 3" 316SS column containing the zeolite (small glass wool plugs were used at both ends of the 1/8" column to hold the zeolite). The column of zeolite was connected directly to the entrance of the TCD.

To assess the moisture capacity of the zeolite, approximately 0.2 grams of the material was activated in the GC (350C for approximately 17 hours) using the packed column arrangement and a small flow of dry helium. The activated zeolite was then cooled to 100C and saturated by the injection of small aliquots of water. The zeolite was then allowed to equilibrate at 100C until the amount of moisture eluting from the sieve was considered to be insignificant (typically 1 to 3 hours). The moisture eluting from the sieve was followed by monitoring the TCD sensor output.

3.5.2.1 Experimental Procedure (Cont'd)

After equilibration at 100C, the sieve was rapidly heated to 350C and the amount of water desorbed from the sieve was measured by integration of the signal from the TCD. The adsorption/ desorption process was repeated with the zeolite sample to examine the influence of multiple activation cycles on the sieve performance.

A similar evaluation was conducted on the Union Carbide 13X zeolite.

In addition to the chromatographic studies, the zeolites were also examined using thermal gravimetric analysis (TGA) techniques. A total of six samples were analyzed. The thermal analysis involved heating the sieve at a temperature of 45C for 30 minutes, ramping the temperature to 200C at a rate of 25C/min, holding the temperature at 200C for two hours and then ramping the temperature to 350C (25C/min) and holding at that temperature for another two hours. The weight loss at each of the temperature plateaus was then used to define the adsorption/ desorption characteristics of the sieves. The 6 samples that were analyzed by TGA are listed below:

DESCRIPTION OF SAMPLES ANALYZED BY TGA

NO.	SAMPLE	STATUS	TREATMENT
I	Residue	Unactivated	Equilibrated at Room Conditions
II	Residue	Activated	Equilibrated at Room Conditions
III	Residue	Activated	Equilibrated over H_2O
IV	13X	Unactivated	Equilibrated at Room Conditions
V	13X	Activated	Equilibrated at Room Conditions
VI	13X	Activated	Equilibrated over H_2O

3.5.2.2 Chromatographic Results

Initially, the adsorption characteristics of the zeolites were to be studied by measuring the amount of moisture trapped on the zeolite upon successive injections of water at a temperature of 40C. The amount of adsorbed moisture was to be estimated by subtracting the amount of moisture which eluted from the actual volume injected. Difficulties were encountered with this procedure in that temperature and adsorption/desorption equilibration factors caused extensive broadening and tailing of the moisture peak, thus making quantification of the moisture peak unreliable. Elevation of the GC temperature to 100C improved the peak shape somewhat; however, the accuracy of the integration method was still inadequate.

In light of these results it was decided to estimate the adsorption capacity of the zeolites by saturating the zeolites at a temperature of 100C, allowing the zeolite to equilibrate and then desorbing the remaining moisture by elevating the temperature to 350C. Using this procedure, the peak shape of the desorbed moisture was improved and more reliable estimations could be obtained.

During the GC study it was determined that a calibration of the TCD moisture response was required for each zeolite and that the response was influenced by the temperature of the GC oven. The calibrations for the zeolites were established by saturating the particular zeolite and then injecting a known amount of additional water into the GC. Assuming that all of the moisture eluted from the zeolite, the corresponding peak area was used to determine the TCD response factor. This calibration method was performed for GC oven temperatures of 100C and 350C (temperature of adsorption and desorption) for both zeolite samples.

The results of the calibrations are shown diagramatically for both samples in Appendix II. The response factors for the various temperatures and zeolites was not expected to vary as much as that observed. The reason for the differences in TCD response can be attributed, in part at least, to the changing shape of the eluting moisture peak. Differences in the packing of the zeolite and the affinity of the zeolite towards moisture served to alter the shape and retention time of the moisture peak and this may have influenced the sensitivity of the TCD.

3.5.2.2 Chromatographic Results (Cont'd)

The integrated results of the desorption experiments are summarized below:

CHROMATOGRAPHIC DESORPTION RESULTS

SAMPLE	DESORPTION CYCLE	WATER INJECTED AT 100C (microliter)	WATER ELUTED AT 100C (microliter)	WATER DESOR. AT 350C (microliter)	VOLUME ELUTED AND DESORBED (%)
Leach Residue	1	40	-	5.2	-
	2	40	34.1	3.4	94
	3	40	34.7	3.5	96
	4	40	35.7	3.5	97
Zeolite 13X	1	40	14	17.9	80
	2	30	8	20.1	94
	3	30	9	21.7	102

The leach residue was saturated and desorbed a total of four times, while the 13X zeolite was cycled through the saturation/desorption process three times. For each desorption experiment the amount of moisture not adsorbed and the amount obtained by the thermal desorption step was noted. This allowed one to monitor a "mass balance" for each experiment. The percentage of the water injected at 100C that was eluted at 100C and desorbed at 350C, is shown in the last column. Ideally this column should read 100%. The values in the above table for the amount of moisture not adsorbed by the zeolite ("WATER ELUTED") were obtained using the 100C calibration curve. The desorption values ("WATER DESORBED") were obtained similarly, using the 350C calibration curve. Since the desorption temperature ranged from 100C to 350C, the values in the table slightly underestimated the actual capacities. Only a small portion of the moisture was observed to desorb at the lower temperatures, so that the errors introduced by the use of the 350C calibration were not considered to be very large.

3.5.2.2 Chromotagraphic Results (Cont'd)

The results obtained for the leach residue were fairly consistent for all four of the desorption cycles. The consistent results, together with the good accountability for the total amount of injected water, express a degree of reliability for the method. Based on the amount of zeolite used in the experiments (0.22g) and the initial moisture content of the zeolite (measured to be 5.7wt%), the average amount of desorbed moisture from the four cycles (3.9 microlitres) corresponded to a dry weight capacity of 1.9wt%.

The three 13X desorption experiments also yielded fairly consistent desorption data. The average amount of desorbed moisture, 19.9 microlitres, corresponded to a dry weight moisture capacity of 13.6 wt% (amount of 13X zeolite used was 0.15g with an initial moisture content of 2.5 wt%).

The "mass balance" for the 13X experiments was not as good as that obtained for the leach residue experiments. The reason for this would appear to be due to the non-linear TCD response curve which was obtained for the 13X at 100C. The affinity of the zeolite for moisture resulted in extensive peak tailing at 100C and this did not allow for accurate peak integrations.

To ascertain if indeed the 13X zeolite sample had a 20 microlitre capacity for water, the third experiment was conducted by first injecting 20 microlitres of water at 100C. The additional 10 microlitres (for a total of 30 microlitres) was injected subsequently. The TCD sensor output was monitored for two hours after the 20 microlitre injection and no moisture was observed eluting from the zeolite. The injection of the additional 10 microlitres of water resulted in a measured elution of 9 microlitres. The fact that no moisture was detected after the 20 microlitre injection confirmed the relatively high moisture affinity of the zeolite 13X.

3.5.2.3 Gravimetric Results

In view of the difficulties that were observed in obtaining quantitive desorption data with the GC method, gravimetric thermal analysis (TGA) was also performed on the zeolites.

Six samples were analyzed as noted in Section 3.5.2.1. The activated zeolite samples used in the TGA study were heated in an oven at a temperature of 350C for 17 hours. The samples that were exposed to "room conditions" were placed in a petri dish and left out in the open for a minimum of ten days prior to analysis. The samples equilibrated over water were supported in a desiccator containing 1" of water and were also allowed to equilibrate for a minimum of ten days.

3.5.2.3 Gravimetric Results (Cont'd)

The results of the TGA studies, showing the percentage weight loss from the samples, along with the calculated moisture capacities, are tabulated below. The data has been corrected for buoyancy effects, caused by changes in the density of the air in the sample chamber. The moisture capacities have been calculated by converting the corrected 350C weight loss data to a dry basis x/(1-x) .

TGA RESULTS ON LEACH RESIDUE AND ZEOLITE 13X

SAMPLE	NO.	WEIGHT LOSS (WT%) 45C 40 MIN	200C 166 MIN	350C 292 MIN	MOISTURE CAPACITY (Wt %)
Leach Residue	I	0.2	3.0	5.1	5.4
	II	0.2	1.9	2.6	2.7
	III	8.6	10.8	13.4	15.5
Zeolite 13X	IV	1.0	17.0	21.0	26.6
	V	1.1	17.0	19.8	26.7
	VI	2.8	19.8	23.7	31.1

NOTE: Above data has been corrected for buoyancy, as follows:

Temperature (C)	Correction (%)
45	0.3
200	0.94
350	1.30

For example, if the measured weight loss at 350C is 1.3%, then the corrected loss is 1.3 + 1.3 = 2.6%

3.5.2.3 Gravimetric Results (Cont'd)

In general, the zeolite moisture capacities, as measured by TGA, tended to be in agreement with the chromatographic results. The slightly higher moisture contents observed using the TGA method were a result of measuring total moisture content of the zeolite starting from ambient temperature (as opposed to 100C with the chromatographic method).

The moisture capacities measured by TGA for the 13X zeolite were in good agreement with the reported equilibrium value of 26wt%, while the moisture data obtained for Samples I and II (5.4% and 2.7%, respectively) agreed well with the values determined using the chromatographic method (i.e. 5.7% for the raw zeolite and 1.9% for the activated zeolite as discussed in Section 3.5.2.2).

Although the leach residue showed some appreciable moisture uptake when equilibrated over water (moisture capacity of 15.5wt% for Sample III), the moisture was very loosely adsorbed, as evidenced by the loss of 8.6wt% during the 45C stabilization period.

3.5.2.4 Conclusions

Both the chromatographic and gravimetric data indicate that the leach residue has a significantly lower capacity for adsorbed moisture when compared to the commercial 13X zeolite from Union Carbide. Based on the TGA results, the residue adsorbed only 2.7wt% moisture following activation, whereas the 13X zeolite adsorbed 26.7wt% (Section 3.5.2.3).

Although the zeolites were evaluated by studying only the desorption characteristics of the material, the information obtained appeared to be decisive. The leach residue demonstrated an affinity for moisture in only one sample (where the material was equilibrated over water in a sealed container). The TGA results for this sample indicated that the water was very loosely bound to the zeolite surface (Sample III in Section 3.5.2.3).

The difficulties encountered with the chromatographic method during calibration of the TCD response factor and peak integration lead one to believe that the gravimetric data is more accurate and that the method is, therefore, more appropriate for evaluating moisture capacities of zeolites. The chromatographic method may, on the other hand, be more appropriate for zeolite evaluations which involve the adsorption/desorption of more volatile components.

3.5.2.4 Conclusions (Cont'd)

It would appear from the results of this study that the leach residue does not have sufficient moisture capacity for it to be of any commercial significance. In view of the zeolite's low affinity for moisture and large pore size, it is not likely that the zeolite would have any commercial value as a molecular sieve for adsorbing most non-polar and polar components.

The above results serve to confirm the conclusions drawn when the specifications for microsieve application was reviewed in Section 3.2.4.2. Two important characteristics of microsieve materials have not been satisfied; namely a large surface area in the 700 to 800 m^2/g range and a pore size between 3 and 10 Angstroms.

3.5.3 Plastic Filler Testing

The leach residue was tested for its filling characteristics by using it to prepare a 30% filled polypropylene (PP) composite, and performing a variety of tests to compare the properties of the filled and unfilled polymer.

The polypropylene resin used in the test was Himont Pro-Fax 6331 homopolymer. The preparation procedure and test results are discussed in the following section.

3.5.3.1 Experimental Procedures

Preparation of Filled Compound

Resin/filler mixtures were tumble-blended in 1 kg batches with 30% filler by weight.

Compounding was achieved using an Arburg Albrounder 221E/150 injection moulding machine. The blends were moulded at 220C, then the mouldings cut into small sections and ground into coarse granules using a Wiley mill. The first pass granules were remoulded in the same way once more, and again ground to give a second pass granular compound ready for test specimen moulding.

Unfilled polypropylene was also put through this two pass treatment to give it the same thermal history.

3.5.3.1 Experimental Procedures (Cont'd)

Preparation of Test Samples

Test specimens were prepared by injection moulding under the following conditions:

- Plasticizing Cylinder Temperatures	
- Feed Zone	220C
- Metering Zone	220C
- Nozzle Percentage Heating	45%
- Injection Hydraulic Pressure	650 psi
- Back Hydraulic Pressure	200 psi
- Injection Speed	4 machine units (moderately fast)
- Screw Speed	170 rpm
- Shot Size	5.75 machine units
- Mould Temperature	30C

Methods of Testing

(1) Notched Izod impact strengths were measured in accordance with ASTM D256.

(2) Flexural moduli were measured in accordance with ASTM D790, Method I - Procedure A. Specimens measuring 5 inch x 1/2 inch x 1/8 inch were placed on a 2.0 inch support span and tested at a speed of 0.05 inches/minute.

(3) Tensile yield strengths, 1% secant moduli, and ultimate elongations were measured in accordance with ASTM D638. Type I specimens were tested with the aid of strain gauge extensometers under the following conditions: speed of testing, 2 inches/minute; gauge length, 2 inches (filled PP) and 1 inch (unfilled PP).

3.5.3.1 Experimental Procedures (Cont'd)

Methods of Testing (Cont'd)

(4) Oxidation induction temperatures (OIT) were determined according to ASTM D3350, except specimens were cut using a sharp blade to obtain cross sections through 1/2 inch x 1/8 inch thick moulded bars.

The analysis was carried out using a Dupont 910 Differential Scanning Calorimeter (DSC) and a 9900 programmer.

Copies of the OIT scans can be found in Appendix II.

(5) Heat deflection temperatures were measured in accordance with ASTM D648. Testing was conducted at a 264 psi stress.

(6) Melt viscosities and storage and loss properties were determined using a Rheometrics RDA-700. Injection moulded bars were used as the test specimens. Sections from the bars were cut and then tested at 189 - 190C in the frequency sweep mode. Appendix II contains viscosity (ETA), storage modulus (G'), and loss modulus (G") curves plotted against frequency.

3.5.3.2 Experimental Results

The results for the tests described in the previous section are summarized below. The results shown are the averages for a number of determinations. Where appropriate, the average value and standard deviation will be given. The results for unfilled and 30% filled PP are shown side by side for comparison. The actual data can be found in Appendix II.

AVERAGE TEST RESULTS FOR POLYPROPYLENE FILLED WITH LEACH RESIDUE

TEST	UNFILLED PP (AVG. ± STD DEV)	30% FILLED PP (AVG. ± STD DEV.)
Notched Izod Impact Strength (ft-lb/in)	0.43 ± 0.04	0.31 ± 0.07
Tangent Flexural Modulus (10^{-3}psi)	166 ± 3	270 ± 4

3.5.3.2 Experimental Results (Cont'd)

AVERAGE TEST RESULTS FOR POLYPROPYLENE FILLED WITH LEACH RESIDUE (Cont'd)

TEST	UNFILLED PP (AVG. ± STD DEV)	30% FILLED PP (AVG. ± STD DEV.)
Tensile Properties:		
- 1% Secant Modulus (10^{-3} psi)	209 ± 7	282 ± 7
- Yield Strength (psi)	4,828 ± 33	3,744 ± 20
- Ultimate Elongation (%)	>500	3.69 ± 0.66
Oxidation Induction Temperature (C)	218.3 ± 0.0	204.2 ± 0.9
Heat Deflection Temperature	55 ± 3	64 ± 2

3.5.3.3 Discussion of Results

The addition of 30% of powder filler to the polypropylene had an effect on the rheological properties of the resin. The viscosity and moduli increased. At a frequency of 10 rad/s the following increases occurred: viscosity, 16.9%; storage modulus, 1.77%; and loss modulus, 21.7% (Appendix II).

3.5.3.3 Discussion of Results (Cont'd)

Mechanical properties of moulded specimens were affected to varying degrees. Impact and tensile yield strengths dropped by approximately 25%. However, the drops were about the same as those experienced when commercial fillers are used (Section 3.2.5.4). On the other hand, flexural and tensile moduli increased by roughly 60% and 40% respectively. Similar increases in flexural modulus are obtained with calcium carbonate and glass spheres (Section 3.2.5.4). Ultimate elongation was greatly reduced. This is typical behavior for a stiff filler that is well bonded to the matrix.

Heat deflection temperature (HDT) testing showed the filled sample is more resistant to distortion under load at elevated temperatures. This is consistent with a material that is stiffer at room temperature.

The oxidation induction temperature (OIT) results indicated the filled polypropylene was less thermally stable than the unfilled material. This may have been the result of transition metal ions in the filler catalyzing oxidation reactions. A cleanup step, possibly a chelation type stabilizer package could alleviate this problem.

Scanning electron microscopy (SEM) micrographs were taken of the filled mouldings at two stages of their compounding. "Second pass" mouldings and final specimen mouldings were viewed with attention paid to the fracture surfaces. The second pass mouldings showed reasonably good particle dispersion and bonding to the matrix. The final mouldings showed improved dispersion and very good bonding. The SEM micrographs are presented in Appendix II.

The behavior of the 30% (weight) filled polypropylene was essentially as expected for any approximately spherical filler at this volume loading. It exhibited normal wet-out compounding and moderately good interfacial adhesion to the matrix. The only negative aspect of this material compared to calcium carbonate, for example, was a loss in oxidative stability. This could be corrected at modest cost.

3.5.3.3 Discussion of Results (Cont'd)

With the question of usability being answered in the affirmative, other applications should be considered. Outgassing was observed. If the material has appropriate pore sizes it might be used as a carrier for liquid additives, such as odorants, insecticides or repellants. Such liquids are generally difficult to add to plastics.

If the binding of water is strong enough, the use of this material in sheet moulding compounds should be explored. Trace amounts of free water introduced by calcium carbonate used in SMC formulations, or by atmospheric contaminations, cause adverse changes in application and maturation viscosities. Substitution of a water trapping agent that is chemically inert for the CaO presently used should be evaluated. It should also be noted that small surface area and large pore size precluded the use of the leach residue as a suitable adsorbent in microsieve applications (Section 3.5.2.4). The adsorbed moisture was weakly bound to the leach residue when compared to commercial zeolites. This recommendation should therefore be approached with caution.

4.0 CONCLUSIONS AND RECOMMENDATIONS

(1) The major phase of the leach residue from the Carbovan process is a zeolite material. The activity of this material for the conversion of a synthetic gas oil to gasoline is comparable to a clay catalyst, but less than a commercial FCC catalyst (Section 3.1). The purpose of the project was therefore to explore the potential of the leach residue as a low cost FCC catalyst.

(2) Zeolites can occur naturally in the environment. However, synthetic zeolites that are prepared under carefully controlled conditions are preferred by industry for use as high purity specialty chemicals. The major fields of application of synthetic zeolites are detergent building, catalytic cracking, and microsieve adsorption. The zeolite specifications for these fields are tabulated in Sections 3.2.2.2, 3.2.3.8 and 3.2.4.2 respectively.

(i) **Detergent Specifications:**

Zeolite A content	- 85% minimum
Particle Size	- 4 microns maximum
Cation Exchange Capacity	- 255 mg $CaCO_3$/g minimum
Dissolved Metal Ion	- 200 ppm maximum

Usage of zeolite A to remove calcium and magnesium cations should continue to grow as legislation banning sodium tripolyphosphate is introduced.

(ii) **Catalyst Specifications:**

Fluidized-Bed Catalytic Cracking	- faujasite
Hydrocraking	- faujasite mordenite
Isomerization	- mordenite ZSM-5
Synfuel	- ZSM-5
NO_x Treatment	- faujasite mordenite

4.0 CONCLUSIONS AND RECOMMENDATIONS (Cont'd)

FCC Catalyst	- 700 ppm Fe 0 ppm V, Ni,Cu 335 m^2/g Surface Area 0.60 cm^3/g Pore Volume 62 microns Particle Size 75 - 85% Conversion Rate

Catalytic cracking is the largest user of zeolite catalysts. Growth rate should be around 3 to 5%/year. The market is stable but competition is stiff.

(iii) **Microsieve Specifications:**

Zeolite	- faujasite
Pore Size	- 3 to 10 Angstroms
Surface Area	- 700 to 800 m^2/g

Growth rate is predicted at 5%/year. Competition is also severe.

(iv) **Filler Specifications**

Particle Size	- 3 to 30 microns
Surface Area	- 0.1 to 20 m^2/g

The leach residue must compete against calcium carbonate and talc for use as plastic filler.

(3) The properties of the leach residue are tabulated in Sections 3.3.1, 3.3.2 and 3.3.3.

(i) The average particle size of 14 microns is too small for catalyst application and too large for detergent building. It was however, in the middle of the size range for fillers. Application of the residue as a filler material is therefore possible.

4.0 CONCLUSIONS AND RECOMMENDATIONS (Cont'd)

(ii) The small surface area (38 to 59 m^2/g), low pore volume (0.08 to 0.18 cm^3/g) and large pore diameter (83 to 121 Angstroms) preclude application of the residue in catalysts and detergents.

On the other hand, the pore and surface characteristics of the residue make it suitable for application as a filler.

(iii) The high carbon content of the residue probably results in a partially coked catalyst with lower activity. The carbon content should therefore be reduced.

(iv) The metals content of the residues was very high, especially sodium, iron, vanadium, nickel and copper. A partially poisoned catalyst of low activity could therefore be expected. The high contents of calcium and magnesium render the residue unacceptable for detergent application. The high metals content could also adversely affect use of the residue as a filler material. The metals content should therefore be reduced to acceptable levels during the leaching or through subsequent processing.

(v) The bulk phase of the feed material (flotation tails) to the leaching process was determined to be mainly amorphous, while that of the leach residue was zeolitic. Thus, leaching was accompanied by the crystallization of the amorphous phase to the zeolite, analcime. Unfortunately, the faujasite structure is needed for detergent, catalyst and microsieve applications. The conversion to this type of zeolite should be investigated as an extension of the leaching process.

4.0 CONCLUSIONS AND RECOMMENDATIONS (Cont'd)

(4) Leach residue samples were tested for FCC catalyst application by SRC. The aim of the tests was to obtain conversion rates that are comparable to commercial catalysts. The results (Section 3.4.1) indicated that:

(i) The conversion rate for the zeolite residue was only marginally better than for the amorphous flotation tails. Crystallization of the flotation tails to the zeolite phase during the leaching process should be investigated more closely.

(ii) The conversion rate was not improved by decoking the residue and mixing it with sand. The sand might, however, be useful in reducing pressure drops caused by the small particles of the residue.

(iii) The conversion rates for the current tests were significantly lower than for the preliminary tests performed in 1986. This can be explained by differences in the gas oil feeds. Catalytic activity of the leach residue was highly sensitive to the purity of the gas oil feed. This explains why the use of a synthetic feed with low impurities in the preliminary tests gave a high conversion rate, and why that rate could not be duplicated during the current tests.

By correcting the results of the current tests for temperature and gas oil feed, the two sets of results were directly comparable (Section 3.4.2).

(iv) Chemical analysis indicated that the leach residue was low on alumina. A significant increase in conversion rate was obtained when the residue was mixed with alumina. This technique should be further investigated as a means of enhancing activity.

4.0 CONCLUSIONS AND RECOMMENDATIONS (Cont'd)

(v) The leach residue was four times as active as sand but only half as active as a commercial FCC catalyst. The factors responsible for the lower activity of the residue include high metals content, small surface area, low pore volume and fine particle size. In its present state, the residue is not suitable for use as an FCC catalyst.

(vi) Analytical and test results both indicate that major chemical and physical changes are needed before the activity of the residue could compete with commercial FCC catalysts. However these changes could be costly and make the residue uneconomical. Before heading blindly into an improvement program that might not be commercially viable, it was decided to terminate experimental testing and assess the situation. Recommended is a systematic study of the alternate chemical and physical changes that must be applied to the residue, along with the costs associated with the changes. A residue improvement program could then be prepared that is both technically and economically feasible. Ideally, such a program could also be incorporated directly into the Carbovan process.

(5) The leach residue was tested for application in the detergent, microsieve and filler industry (Sections 3.5.1, 3.5.2 and 3.5.3).

(i) The capacity of the residues to adsorb water hardening ions (calcium and magnesium) was compared to zeolite A. The residues displayed low adsorption capacity for calcium (10 mg Ca/g), compared to zeolite A (70 mg Ca/g). The residue is therefore not suitable for use in detergents.

4.0 CONCLUSIONS AND RECOMMENDATIONS (Cont'd)

(ii) Evaluation of the residue for microsieve application was carried out by comparing the ability of the residue to adsorb moisture against zeolite 13X. Chromatographic (Section 3.5.2.2) and gravimetric (Section 3.5.2.3) results indicated that the residue had a much lower adsorption capacity for water than 13X. Moreover, the water was only loosely bound to the residue surface.

The combination of low moisture affinity, large pore size and small surface area render the residue unsuitable for microsieve application.

(iii) The residue was tested for filler application by preparing a 30% filled polypropylene composite and comparing the composite properties against those of the unfilled counterpart. The mechanical properties of the filled composite were typical for a stiff filler that is well bonded to the polymer matrix. The residue, therefore, performed as well as commercial fillers under mechanical testing. However, the filled composite displayed less thermal stability due, in all likelihood, to the high metals content. Further investigation into the use of the residue for filler applications is recommended, along with simultaneous efforts to reduce the metals content.

APPENDIX I

SRC

ZEOLITE MATERIAL FOR CATALYST TESTING

PETROLEUM DIVISION

SRC

Saskatchewan
Research Council 515 Henderson Drive Regina, Sask Canada S4N 5X1 Phone (306) 787-9400 Telecopy 949-2644

March 26, 1986

Dr. V.I. Lakshmanan
Manager, Mineral Processing and Hydrometallurgy Groups
Ontario Research Foundation
Sheridan Park Research Community
Mississauga, Ontario
L5K 5X1

Dear Dr. Lakshmanan:

Re: **Zeolite Material for Catalyst Testing**

As we discussed on the telephone, SRC has completed the testing of the zeolite material to determine its suitability as a catalyst. With this letter I will provide additional information regarding the details of the testing, the results and the conclusions that can be interpreted from the results.

The catalyst test is called Fluid Cracking Catalysts by Microactivity Test (FCC MAT). The apparatus used is a MAT unit. A schematic of the equipment is provided. Not shown on the diagram is the gas collection and analysis equipment. The procedure we use is based on the ASTM D 3907-80 FCC MAT procedure which is also enclosed. The only deviation from the ASTM procedure is that we often use a variety of reaction temperatures (in this case we used two 482°C and 504°C).

The purpose of the test is to measure the conversion of the gas oil feedstock (boiling range 345-525°C) to gasoline (material boiling less than 216°C). Other factors sometimes measured are the coke factor (the amount of material polymerized to coke) and gas factor (amount of gas made, includes hydrogen and hydrocarbons C_4 and lighter). The coke and gas factor are measures of the catalyst's selectivity and are not that important at this stage.

. . 2

We received three samples of zeolite material from ORF. The only difference between the first two was that the second sample had not been dried. The third sample had been treated a second time at ORF. The following table summarizes the results of our MAT tests.

MAT TEST RESULTS

Sample Description	Reaction T °C	Conversion (wt.%)	Volume (ml)
Gas			
1. No. 1, as received	482	43.4	40
2. No. 1, decoked	482	20.7	11
3. No. 2, dryed	482	41.1	97
4. No. 2, dryed	504	47.7	109
5. No. 2, diluted with sand	482	61.0	62
6. No. 3, as received	482	40.0	64

The feedstock used for all cases was a gas oil derived from a conventional light crude typically used at Canadian refineries at this time.

A number of relevant observations were made when the tests were performed. For a typical FCC catalyst test the catalyst must first be decoked in a furnace at 590°C for 3 hours. We decoked some of the catalyst and compared it to the as received material and found it to have a higher activity without decoking. All the remaining tests were done without decoking. Although the first sample appeared dry it still contained a significant amount of water. Initially we thought we had achieved high conversion until the water settled out of the reaction products. All three samples provided similar conversions when tested as received although there is a variation in the gas volume.

We noted that the samples seemed to have a small particle size when compared to commercial catalyst. The average particle size for a typical commercial catalyst is approximately 70 microns. For these samples it was significantly less. Small particle size can cause problems with the MAT unit because the catalyst will pack during the test and the gas oil may not be exposed to sufficient catalytic surface. Higher than normal pressure drops were observed during the experiments indicating some bed packing. For one test we diluted the catalyst with some sand and the conversion improved dramatically to 61%. We have tested the sand by itself to determine if it has any catalytic capability. I will forward these results to you when they are complete.

. . 3

Under similar test conditions a commercial catalyst will convert approximately 60-70% of the gas oil to gasoline. From a conversion point of view this zeolite material has significant potential. However, gas make is quite high, 40-50 mls of gas are normally produced when testing a commerical catalyst. We performed one gas analysis (of the last experiment) and found that the gas was mainly hydrogen. The H_2/CH_4 ratio was approximately three, whereas for a commercial catalyst the ratio is 0.5-1.0. This indicates that some dehydrogenation of the product is occurring, which is not desirable. This problem could be overcome with some additional development work on the zeolite.

The results indicate that there is potential for developing this material into a catalyst. When diluted with the sand it provided conversions similar to natural clays (bentonite) and slightly less than available commercial catalysts. We are willing to provide suggestions into possible improvements should your client wish to pursue development.

If there are any questions regarding the tests, please do not hesitate to contact me at (306)787-9331.

Yours truly,

DSoveran

Douglas W. Soveran
Senior Research Engineer

DS/dh

c.c. R. Ranganathan
E. Ogu

Attachments

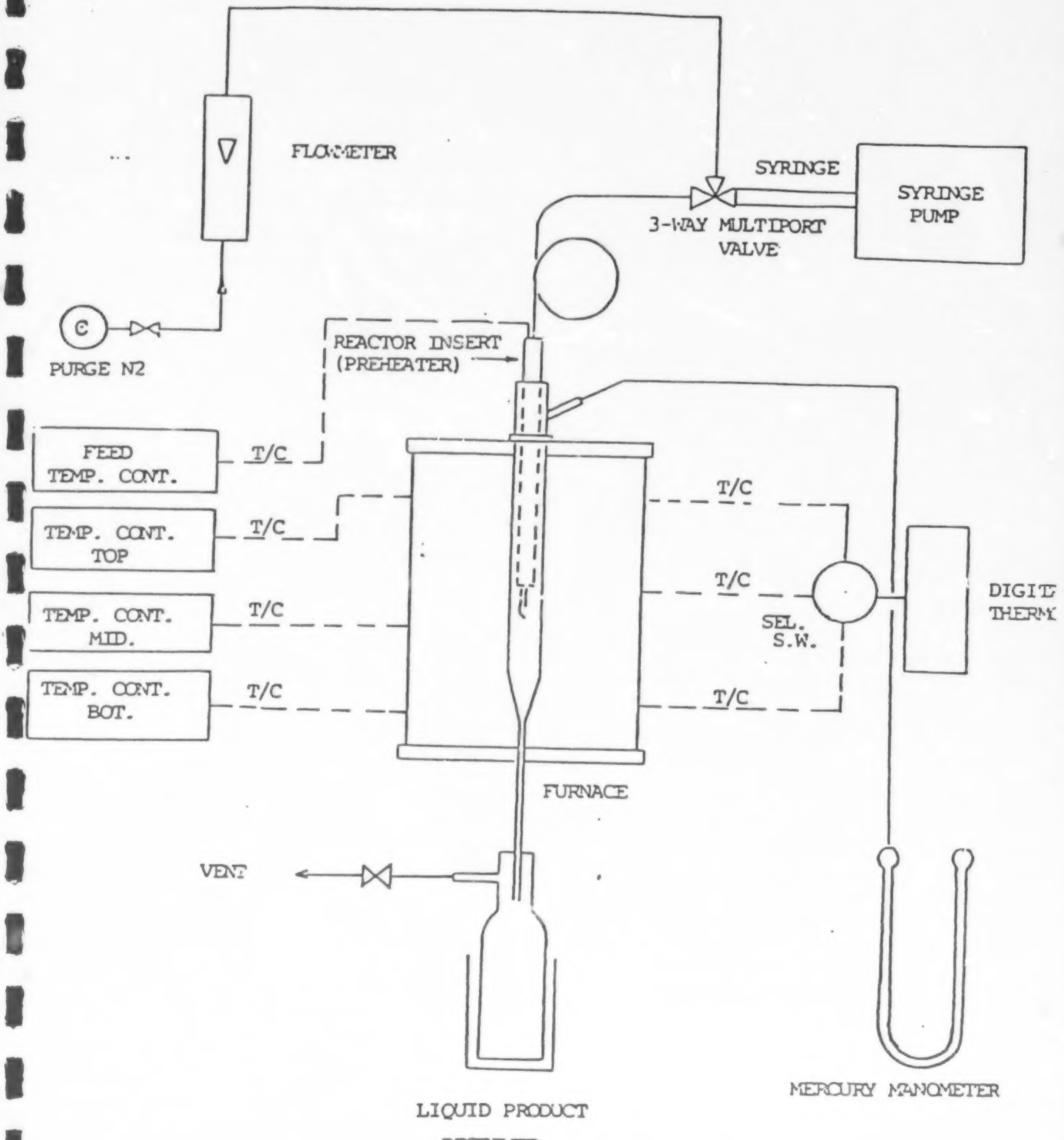
FLOWMETER
SYRINGE
SYRINGE PUMP
3-WAY MULTIPORT VALVE
PURGE N2
REACTOR INSERT (PREHEATER)
FEED TEMP. CONT.
T/C
TEMP. CONT. TOP
T/C
TEMP. CONT. MID.
T/C
TEMP. CONT. BOT.
T/C
T/C
T/C
T/C
SEL. S.W.
DIGIT THERM
FURNACE
VENT
MERCURY MANOMETER
LIQUID PRODUCT RECEIVER

FIGURE 1 - MICROACTIVITY FLOW CHART

Note: This drawing not to scale.

The gas oil samples solidified easily at room temperature. Prior to use in each experimental run, the feed sample was placed in an oven and heated for approximately 10 minutes at 40°C. This simple procedure made it possible to transfer the gas oil into a syringe.

2 Reactor Preparation

Before each experimental run, the reactor was properly rinsed with acetone and dried in air. The reactor feed line as well as the product receiver were prepared in a like manner. The essence was to rid the reactor components of contaminants that might affect the experimental results. While the reactor was being prepared, the furnace was preheated to 482°C (900°F) to establish a steady and stable temperature before inserting the reactor into the furnace. A plug of borosilicate glass wool was inserted into the reactor to serve as the catalyst support. Four grams of the decoked equilibrium catalyst were measured and added in a free flowing manner into the reactor. Following the addition of the catalyst, the reactor was tapped slightly to ensure good radial distribution and another plug of glass wool was positioned above it. The amount of the catalyst required was determined by first establishing the weight of an empty crucible and adding the catalyst to increase this weight by 4 grams. Usually, about 0.03 grams of excess catalyst was added to compensate for any catalyst lost to the surface of the crucible.

3 EXPERIMENTAL PROCEDURE

1 Sample Preparation

The best overall performance of any catalyst used in an FCC operation can be assessed by knowledge of its activity. Activity measures the ability of the catalyst to convert gas oil. Spent or equilibrium catalysts from refinery FCC operations have very limited activity and are continuously regenerated by decoking, i.e. burning off the coke components in the air.

The equilibrium catalysts used in this study were sequentially decoked prior to use. The decoking procedure closely followed the method stipulated by ASTM D3907-80. A shallow bed of the equilibrium catalyst sample in a porcelain crucible was placed in a muffle furnace and heated as follows:

120°±20°C (250°±40°F) for 1 hour,

120°C (250°F) to 590°C (1094°F) for approximately 1 hour,

590°±20°C (1094°±40°F) for 3 hours.

After the five hour decoking period, the catalyst sample was fully regenerated as indicated by its whitish colour. The hot crucible containing the decoked catalyst sample was placed in a desiccator to prevent moisture pickup.

After ensuring the tip of the insert thermocouple was bent directly under the tip of the reactor feed tubing, the insert (preheater) was placed into the reactor. This necessary step ensured proper measurement of gas oil preheat temperature. The position of the reactor feed tube insert above the catalyst bed was adjusted to 10-50 mm. This adjustment prevented the insert thermocouple from touching the catalyst bed thereby ensuring that the catalyst bed temperature was not monitored in favour of the feed temperature.

The reactor, so prepared, was placed in the preheated furnace. The nitrogen feed line was connected to the reactor via the 3-way multiport valve and the reactor purged with 30 ml/min of nitrogen for 30 minutes. Purging the reactor prior to the addition of oil helped to stabilize the reactor temperature. Following the insertion of the reactor into the furnace, the electrical connection on the integral oil feed was made as well as connecting the feed preheat thermocouple.

3 Preparation of Syringe and Liquid Product Receiver

The 10 ml. syringe was filled with the gas oil sample and its weight determined. The nitrogen feed line was temporarily disconnected to enable the gas oil syringe to be connected to the 3-way multiport valve. The syringe thermocouple was placed on the syringe body which was heated to 40°±5°C by a heat lamp. The heat lamp was switched on and off depending on whether the syringe temperature was steady at 40°C or not. A wet ice bath was prepared and installed for the liquid product receiver. This receiver was embedded in the cold bath and connected to a vent or a gas sampling bag depending on the need.

4 Run Conditions

Each experimental run was carried out when the reactor temperature had stabilized at 482°C (900°F). The syringe pump was set to deliver 1.3 grams of the gas oil feed in 75 seconds. When the syringe and reactor temperatures were respectively 40°C and 482°C, the multiport valve was switched from the nitrogen flow to the gas oil feed position. The syringe pump was started to transfer 1.3 grams of the oil feed in 75 seconds. This transfer time was determined using a stop watch. Immediately following the gas oil transfer into the reactor, the nitrogen flow was restarted and the reactor as well as the product receiver purged with 30 ml/min of nitrogen for 15 minutes. This purging was necessary to flush into the product receiver any cracked hydrocarbon fractions trapped in the catalyst bed.

At the end of the nitrogen purge, the liquid product receiver was disconnected from the reactor, sealed, dried and weighed immediately. The liquid product hold-up at the exit port of the reactor was collected by means of a Q-tip and its weight determined. (This substance is regarded as unconverted material and is taken into account when calculating the weight percent conversion of the gas oil).

The amount of the liquid product was determined and then analyzed by gas chromatography using a simulated distillation technique. The essence was to determine the weight percent of hydrocarbons boiling above 216°C. This was subsequently used to calculate the overall measured conversion. A summary of the analytical results is presented in Table 2.

The activity of the equilibrium catalyst used in each calibration experiment was evaluated on the basis of weight percent conversion of the gas oil in the microactivity test (MAT) unit. The weight percent conversion was determined using the following measured conversion formula:

$$\text{Measured conversion, wt\%} = \frac{F - \frac{R \times L}{100} - H}{F} \times 100$$

where:

F = grams of gas oil fed into the reactor

R = weight percent of material boiling above 216°C in liquid product receiver

L = grams of liquid product in receiver

H = grams of liquid hold-up at reactor exit line.

A summary of the results compiled from the measured conversion is shown in Table 2.

APPENDIX II

ORF

FABRICATION OF FCC CATALYSTS FROM SUNCOR FLYASH LEACH RESIDUE

This Appendix exists as a separate self-contained volume.

APPENDIX III

SRC

CARBOVAN FCC CATALYST FABRICATION REPORT

PETROLEUM DIVISION

SRC
Saskatchewan
Research Council 515 Henderson Drive Regina, Sask. Canada S4N 5X1 Phone: (306) 787-9400 Telecopy: 787-8811

April 20, 1988

Dr. I.A. Todd
Project Scientist
Mineral Resources
Ontario Research Foundation
Sheridan Park Research Community
Mississauga, Ontario
L5K 1B3

Dear Iain:

Re: Carbovan FCC Catalyst Fabrication Project

Further to our telephone discussion, the microactivity test (MAT) results for the flyash samples received from you to date with regard to the above project are hereby presented for your review. The tests were performed at 482°C using the same conventional gas oil feedstock. The samples were dried (3 hours, 450°C) prior to testing. As indicated, a few samples were also tested as received. The conversions are the averages of duplicate runs.

Sample	Conversion, wt %	Gas Yield, mL
E58 as rec'd	21.1	30.0
E58	26.9	29.0
E59	21.4	30.0
E60	25.5	6.0
E69 as rec'd	27.6	50.0
E69	28.0	38.5
E70 as rec'd	31.6	54.5
E70	25.2	50.0
E77 as rec'd	29.4	38.5
E77	28.1	39.5

In comparison with commercial FCC catalysts, the flyash samples gave very low conversions. Equally low were the gas yields. Samples E69-E77 performed better than samples E58-E60 in terms of conversions and gas yields.

The small particle size of the flyash inhibits diffusion of the gas oil molecules through the pores resulting in little or no cracking reaction and ultimately to a very low conversion. The use of silica material with the flyash sample did little to alleviate the problem.

The diffusion problem seems to disappear if the reactor is packed with the same quantity of flyash used per experiment and the purge nitrogen passed through it. For this test the reactor is not heated. This indicates that heat causes possible expansion of the flyash material resulting in further blockage of the pores and interstitial spacings.

To improve the poor catalytic performance of the flyash material, the following steps may be considered:

1. The physical and chemical characteristics of the flyash need to be changed. The present surface area of the flyash (~38 m^2/g) in comparison to that of a commercial catalyst (250 m^2/g and higher) is very low. High surface area is desirable for gas oil cracking. The pore volume (0.08 mL/g) is low relative to that of a commercial FCC catalyst (~0.9 mL/g). Both the iron and sodium contents are respectively high at 9.2 and 8.9%. A reduction to about 3% Fe_2O_3 is desirable; 0.6% is preferable. The sodium level must be reduced at about 0.5%.

2. The surface area of a clay-like material may be increased by interlayering with a polymer such as aluminum chlorhydroxide marketed as chlorhydrol by Reheis Chemical Inc. (contact Chris Ponza: (201) 454-1500). The interlayering is carried out as follows:

   Dilute desired quantity of chlorhydrol to desired volume.
   Add flyash (1 g per 2 g chlorhydrol).
   Homogenize slurry and age 1 hr at 60-90°C, holding the slurry at pH = 2-6 with either 3% HNO_3, or HCl.
   Filter, wash thoroughly with hot deionized water, and spray dry or oven dry overnight at 105°C.
   Sodium gluconate may be used to reduce Fe_2O_3 level.

   One concern about pillaring with chorhydrol is the possibility of further collapse of the flyash structure since it is not pure clay.

   The flyash material may be treated with H_2SO_4 or HCl at a moderately high temperature, washed and dried. Finding a way to agglomerate the flyash may help increase the particle size or you may use it as a binder/support for a more active catalytic material.

   The materials produced are calcined for 3 hrs at <500°C.

I trust I have addressssed some of your concerns. However, if you require additional information, please do not hesitate to contact me at (306) 787-9800.

Yours truly,

Eugene Ogu
Research Engineer

EO/dh

c.c. D. Soveran
R. Ranganathan

June 9, 1988

Dr. V. I. Lakshmanan
Manager
Mineral Processing and
Hydrometallurgy Groups
Ontario Research Foundation
Sheridan Park Research Community
Mississauga, Ontario
L5K 1B3

Dear Dr. Lakshmanan:

Re: Carbovan FCC Catalyst Fabrication Project

As requested, attached is a brief status report on Task 5 of the above project. Some suggestions are made to improve the catalytic performance of the flyash. Please do not hesitate to contact me at (306) 787-9800 if you have any concerns.

Yours truly,

Eugene Ogu
Research Engineer

CC: D. Boveran
R. Ranganathan

Catalytic Performance of the Unmodified Flyash Leach Residue

The FCC catalyst evaluation data representing the microactivity test (MAT) results of the unmodified flyash leach residue are described in this status report. Presented in Table 1 is a comparison of the previous (test nos. 1-5) and present (6-15) flyash test data versus typical test results of a commercial FCC catalyst (22-23). Also included in Table 1 are the results of additional flyash MAT tests (16-21) to determine whether some past reults could be reproduced to discern the reasons for discrepancies in some conversions. The physical and chemical properties of a typical flyash material are compared in Table 2 with those of a pillared clay catalyst and a commercial fresh FCC catalyst. This comparison is intended to help determine specific property changes necessary to produce an acceptable flyash FCC catalyst.

Three different flyash samples (Feb/86, Mar/86 and BR-354) were tested in 1986. The Mar/86 sample contained about 50 % water when received and was dried prior to MAT testing. The conversion levels (except for exp. no. WC8-504) averaged about 40 wt % at 482 C reaction temperature and 44 wt % at 504 C. However, a value of 61 wt % conversion was obtained when Mar/86 sample was tested using a synthetic gas oil and sand (to reduce diffusion problems). This result is questionable as explained later in this report.

Six different samples (6-15) were tested in 1987/88. As indicated in Table 1 most of the samples were tested as received (i.e., no drying, decoking or mixing with sand) and also after being dried/decoked and mixed with decoked sand. Each run was performed at the same reaction temperature (482 C) using the same conventional gas oil feed. Compared to previous (1986 sample tests) results, each flyash sample produced a low conversion. Current flyash samples are much lower than a typical commercial FCC catalyst (test no.22) conversion level (65.4 wt %). However, the almost identical conversion results indicate the reproducibilty of the MAT runs. Differences in flyash leach treatment conditions coupled with variability in MAT test parameters can influence the catalytic performance of the sample. Because the MAT tests were carried out under constant operating conditions, it is only logical to attribute the different performance results to differences in the characteristics of the samples. Accordingly, samples E69-E77 performed better than samples E58-E60 in terms of conversions and gas yields. Testing decoked E58 with decoked sand increased the conversion by about six percent relative to testing the sample as received. The decoked and as received E69 produced almost the same conversion result (28 wt %). Decoking samples E70 and E77 resulted in reduced conversions. Sample E70 had the best overall performance when tested as received.

Some past MAT runs were repeated in order to determine the reasons for the low conversions. These are given by the tests numbered 16-21. Test 4 with the 61 wt % conversion was repeated with a synthetic gas oil and yielded about 24 wt. However, when the same test (#16) was repeated using a conventional feed, a value of about 34 wt % was obtained. It could not be determined why the 61 wt % conversion was not reproduced. Test #12 for sample E70 was repeated in test #17. The two results are comparable except that a conversion increase of about 4 wt % (probably due to the higher reaction temperature of 504 C) was obtained for test #17. The catalytic effect of mixing the flyash with sand was determined. Testing just the sand (test #20) yielded 8.6 wt % relative to 8.8 wt % obtained when the material was tested in 1986. Testing at a higher reaction increases the conversion as indicated by tests 22 and 23 of a commercial FCC catalyst.

There is no doubt that the flyash material possesses catalytic properties. If the physical properties of the flyash are compared to an FCC catalyst it is clear that the leach process changes have not made the flyash more typical of FCC catalyst. Table 2 compares the physical and chemical properties of the flyash with those of a commercial FCC catalyst and a pillared clay (bentonite) catalyst. The properties of samples E69 and E70 are comparable to those of E56 and E51 indicated in Table 2.

Table 2 shows that the flyash compared to a commercial zeolite catalyst is low in alumina. It also has respectively high sodium and iron contents of about 9 wt % versus 0.6 wt % for the commercial catalyst. High sodium and iron contents can make the flyash less effective as a catalyst. The vanadium and nickel contents of the flyash are also high and coupled with the vanadium and nickel contents of the gas oil, would be expected to impact negatively on the catalytic performance of the flyash. Comparing the chemical properties of the flyash with those of the clay material also indicate areas where modification is necessary for the flyash to effectively perform as an FCC catalyst. The physical properties indicate that the flyash is extremely low in surface area; 38 m2/g versus 288 and 270 respectively for the commercial and clay catalysts. The surface area of the flyash must be increased considerably for it to yield any high conversion result. The flyash has a small particle size of 15 micronmeter versus 70 micronmeter for the commercial catalyst. The small particle size causes reactant diffusional problems as experienced during the various tests. This small particle size coupled with the low surface area constitutes a major impediment to the effective use of the flyash as a source of FCC catalyst.

Recommendations

The following recommendations are offered to help improve the catalytic performance of the flyash. They are not intended to replace other flyash modifications planned for this project.

1. The physical and chemical characteristics of the flyash need to be changed. The present surface area of 38 m2/g as already pointed out is very low. High surface area is desirable for gas oil cracking. The pore volume is low while the sodium, iron, vanadium, and nickel contents are very high and must be reduced. It may be necessary to determine the properties of the flyash before and after every property modification in order to pinpoint specific property improvement achieved and further modification necessary to obtain the desired catalyst.

2. Reproducible flyash leach residue treatment conditions must be established and followed to produce the material which is to be further modified to generate a flyash catalyst with an expanded surface area.

3. The surface area of a clay-like material may be increased by interlayering with a polymer such as aluminum chlorhydroxide marketed as chlorhydrol by Reheis Chemical Inc. (Chris Ponza: (201) 454-1500). The interlayering is performed as follows:

Dilute desired quantity of chlorhydrol to desired volume.
Add flyash (1 g per 2 g chlorhydrol).
Homogenize slurry and age 1 hr at 60-90°C, holding the slurry at pH = 2-6 with either 3% HNO_3, or HCl.
Filter, wash thoroughly with hot deionized water, and spray dry or oven dry overnight at 105°C.
Sodium gluconate may be used to reduce Fe_2O_3 level.

One concern about pillaring with chorhydrol is the possibility of further collapse of the flyash structure since it is not pure clay.

4. The flyash may also be treated with H2SO4 or HCl at a moderately high temperature, washed and dried. Finding a way to agglomerate the flyash may help increase the particle size.

5. The physical and chemical properties of the specific flyash material to be MAT tested must be made available to us to help interprete the yield results. It is desirable that drying/calcination of the finished product be carried by the person doing the MAT work.

TABLE 1. CARBOVAN FCC CATALYST FABRICATION PROJECT

Flyash MAT Performance Comparison

Test No.	Sample I.D.	Exp. I.D.	Feed	Catalyst (g)	Catalyst Treatment	Sand (g)	Sand Treatment	Rx. Temp °C	Conversion (wt %)	Gas Yield mL
1	Feb/86	FD20482	Conv.	3	Decoked, ASTM 120-590°C, 5h	0	-	482	43.4	40
2	Mar/86 Pilot Leach Tails	C504	Conv.	4	Dried overnight 120-150°C	0	-	504	41.1	97
3	Mar/86	D504	Conv.	4	Sample for exp. #C504 further dried 1.5 h at 350°C	0	-	504	47.7	109
4	Mar/86	WCS-504	Synthetic	3	Dried 1.5 h @ 350°C	1.5	Decoked 5h at 650°C	504	61.0	62
5	BR-354	BR-4822	Conv.	4	No treatment Tested as rec'd	0	-	482	40.0	64
6	E58 CAUSTIC	E58	Conv.	3	Tested as rec'd	0	-	482	21.1	30
7	E58	E58DS	Conv.	3	Decoked 3h @ 450°C	1.5	Decoked 3h @ 450°C	482	26.9	29
8	E59 CARBONATE	E59DS	Conv.	3	-do-	1.5	-do-	482	21.4	30
9	E60 3:1 FLOAT TAILS	E60DS	Conv.	4	-do-	1.5	-do-	482	25.5	6
10	E69 ESP/CARB.	E69	Conv.	4	Tested as rec'd	0	-	482	27.6	50
11	E69 " "	E69DS	Conv.	3	Decoked 3h @ 450°C	1.5	Decoked 3h @ 450°C	482	28.0	38.5
12	E70 EGR· Al_2O_3	E70	Conv.	4	Tested as rec'd	0	-	482	31.6	54.5
13	E70 " "	E70DS	Conv.	3	Decoked 3h @ 450°C	1.5	Decoked 3h @ 450°C	482	25.2	50.0
14	E77 ESP/CAUSTIC	E77	Conv.	4	Tested as rec'd	0	-	482	29.4	38.5
15	E77	E77DS	Conv.	3	Decoked 3h @ 450°C	1.5	Decoked 3h @ 450°C	482	28.1	39.5
16	Mar/86	RC504	Conv.	3	-do-	1.5	Decoked 5h @ 650°C	504	33.8	42.0
17	E70	E70504C	Conv.	4	Tested as rec'd	0	-	504	35.7	72.0
18	Mar/86	C-5041	Conv.	4	Dried 1.5h @ 350°C	1.5	-	504	33.5	30.0
19	Mar/86	C5042	Conv.	4	Decoked 6h @ 350°C	0	-	504	32.9	32.0
20	Sand	S504C	Conv.	0	-	8	Decoked 5h @ 650°C	504	8.6	18.0
21	Feb/86	T-504C	Conv.	4	Al chloride Dried 20h @ 120°C Further dried 1h @ 350°C	0	-	504	38.5	90.5
22	Commercial Equilibrium	B482	Conv.	4	Decoked 5h @ 120 -590°C	0	-	482	65.4	-
23	-do-	B504	Conv.	4	-do-	0	-	504	72.3	-

Table 2 - Comparison of Physical and Chemical Properties

	Commercial FCC Catalyst (Fresh HEZ-55)	Flyash Material (Unmodified)	Clay (Pillared)
Chemical Analysis		(E56)	
Al2O3, wt %	58.0	22.6	26.2
SiO2, wt %	36.0	42.5	54.5
TiO2, wt %	2.4	3.1	-
Na2O, wt %	0.6	6.9	0.4
Fe2O3, wt %	0.6	9.2	4.6
CaO, wt %	-	2.0	0.2
MgO, wt %	-	1.2	2.4
K2O, wt %	-	0.3	0.8
V, ppm	<150	2800	-
Ni, ppm	<150	6600	-
Zeolite, wt %	20.0	-	-
REO, wt %	1.8	-	-
Physical Analysis		(E81)	
SA, m2/g	288.0	38.2	270.0
PV, mL/g	0.4	0.1	0.2
BD, g/mL	0.9	0.7	-
APS, micronmeter	70.0	15.0	-

APPENDIX IV

SRC

SYNTHETIC AND CONVENTIONAL GAS OILS

CHARACTERISATION OF SYNTHETIC GAS OILS

	Syncrude	Suncor	ARDS*
API Gravity, 15/15°C	17.9	19.3	24.5
Specific Gravity	0.9470	0.9385	0.9068
Pour Point, °C	-1.0	5.0	14.0
Sulphur, wt %	0.48	0.72	0.10
Carbon, wt %	87.7	85.5	84.8
Hydrogen, wt %	11.8	11.8	12.6
C/H Ratio	7.4	7.2	6.7
Refractive Index, 20°C	1.5280	1.5250	1.5026
Con. Carbon Residue, wt %	0.08	0.03	0.03
Rams. Carbon Residue, wt %	0.13	0.10	0.02
Metals: ppm			
Sodium	6.02	13.4	4.72
Vanadium	1.19	1.62	2.18
Iron	0.82	0.39	0.21
Nickel	0.29	<0.07	<0.07
Copper	0.25	0.21	<0.07
TBP Distillation:			
Volume Percent	**Temperature, °C**		
IBP	318	319	315
10	349	346	351
30	380	371	378
50	410	393	400
70	442	418	422
90	487	450	447
FBP	561	493	495
IBP - 204°C, Vol %	-	-	-
204°C - 343°C	7.0	8.0	6.0
343°C - 525°C	89.8	92.0	94.0
525°C+ Residue	3.2	-	-
Hydrocarbon Type, wt %			
Aromatics:			
Mono	23.8	23.8	26.5
Di	13.8	22.7	12.1
Tri	5.7	0.2	1.0
Tetra	4.7	0.3	0.2
$\geq$ 5-ring	1.1	3.2	0.1
Total Aromatics	49.1	50.2	39.9
Saturates	45.6	47.2	57.0
Polar Compounds	6.9	1.8	3.7

* This sample is representative of the synthetic gas oil used in test number 5 of the preliminary FCC Mat tests (see Section 3.1).

CHARACTERISATION OF CONVENTIONAL GAS OILS

Feed Identification	**921**	**1012**	**1122**	**1213**
Gravity, °API	25.3	25.8	24.9	26.9
Total Carbon Residue, wt %	0.37	0.32	0.29	0.25
Sulphur, wt %	0.79	0.76	0.89	0.68
Pour Point, °C	32	31	27	31
Metals, ppm				
Nickel	0.06	0.12	0.08	0.06
Vanadium	0.05	0.06	0.06	0.07
Sodium	3.91	5.19	3.22	4.31
Copper	0.25	0.54	0.24	0.29
Iron	0.77	0.49	0.41	0.52
Feed Distillation (TBP), °C				
IBP	202	194	178	178
10	302	301	268	271
30	356	356	341	336
50	401	399	384	381
70	451	451	434	437
90	516	518	504	510
FBP	593	593	582	593

* This sample is representative of the conventional gas oil used in both the preliminary and current FCC MAT tests.

The preceding two tables and the following text has been excerpted from the following SRC report, "Evaluation of Upgrading Characteristics of Saskatchewan EOR Feedstocks and Distillate Fractions", March 1987.

Discussion of Synthetic Gas Oil Properties

Three different synthetic gas oils were evaluated. The Suncor gas oil was derived from a synthetic crude produced after hydrotreating and delayed coking of Athabasca bitumen. Similarly, the Syncrude sample was derived from a synthetic crude produced after hydrotreating and fluid coking of Athabasca bitumen. The third gas oil was derived from a Saskatchewan heavy crude upgraded in a fixed bed atmospheric residual desulphurization (ARDS) pilot plant (from NewGrade Energy).

Prior to MAT testing, the three gas oils were distilled to provide a gas oil fraction with the boiling range approximately 345-525°C. Figure 1 shows their distillation relationships. The properties of the samples were determined. Separation of the individual sample into different hydrocarbon types was performed in the CANMET Energy Research Laboratories. Some of the properties of the gas oils are given in Table 1.

There are many different variables that require careful balancing for proper control and operation of an FCC unit. Feed quality is an important varibable and individual feed characteristics are a measure of its quality. The behaviour of a feed in a cracking reaction coupled with the cost of processing it and the economic value of its products are all governed by the characteristics of the feed.

Important characteristics of the three gas oils which could determine their crackability and potential processing problems are easily discernible in Table 1. The Syncrude gas oil (946 kg/m^2) was the heaviest sample evaluated followed by Suncor gas oil (938 kg/m^3). The ARDS sample (906 kg/m^2) was comparactively light. This indicates that Syncrude was the most aromatic and the ARDS the least aromatic. From Table 8, which contains density values for the undistilled samples, it can be seen that the change in density value for each sample was due to a change in the boiling range. The distillation of each sample effectively eliminated the light ends (the portion boiling up to 315°C). With respect to the initial boiling points, Syncrude and Suncor gas oils had almost the same value (318°C). The ARDS sample had a slightly lower initial boiling point (315°C). There was a significant difference in the spread of the final boiling points of the gas oils. The Syncrude sample, with an end point of 561°C, had about 90 vol % of the material boiling in the range 343-525°C. The distillation residue (525°C+) accounted for about 3%. In comparison, the Suncor and ARDS had a much lower average final boiling point of approximately 494°C. However, these two samples had a much larger volume (93%) of material with a boiling range of 343-525°C+. There were no 525°C+ residues in the Suncor and ARDS samples.

The coke-forming propensities in any catalytic cracking event can generally be correlated to high-boiling aromatic and carbon residue contents of the feed being processed. The Syncrude and Suncor gas oils contained the same amount of hydrogen (11.8 wt.%) and are more aromatic than the ARDS sample with a hydrogen content of 12.6%. Also, notice the lower total aromatic content (39.9%) for the ARDS sample and about 49% for the Syncrude and Suncor samples. Mono- and di-aromatics contributed more to the total aromatic contents of the samples than the polyaromatics (tri-, tetra-, $\geq$5-ring). Because ARDS was less aromatic (more saturated), it would be expected to crack more readily and yield a greater coversion. The carbon residue of a feedstock (a measure of its coke-producing nature) can be related to either the Conradson or Ramsbottom carbon content. Gas oil having a carbon residue of 0.5% is usually considered a problem. In this study, the Ramsbottom carbon residue content of the Syncrude sample was 0.13%. Suncor had 0.10% while ARDS had the lowest value of 0.02%.

Metal contaminants in the FCC feed can cause serious processing problems if they deposit on the cracking catalyst. The presence of iron, vanadium, nickel and copper causes undersirable dehydrogenation reactions. Of the three gas oils evaluated, the ARDS sample had the highest vanadium content of 2.18 ppm. Suncor contained 1.62 ppm while Syncrude's content was lowest with a value of 1.19 ppm. Nickel was virtually absent in the Suncor and ARDS samples. Sodium generally has a deleterious effect on the zeolite structure of the cracking catalyst. The Suncor gas oil had a high sodium content (13.4 ppm) followed by Syncrude (6.02) ppm.

Sulphur is undersirable in cat cracker feed because it causes corrosion of equipment and difficulty in treating products. The ARDS sample had the lowest sulphur content (0.1 wt.%) while the value (0.72 wt.%) in the Suncor sample was the highest. The low sulphur content of ARDS gas oil was a result of high severity desulphurization hydrotreating.

APPENDIX II

ORF

FABRICATION OF FCC CATALYSTS FROM SUNCOR FLYASH LEACH RESIDUE

A Part of The

FINAL REPORT

PREPARED BY

THE CAMBRIAN ENGINEERING GROUP LIMITED

FOR CARBOVAN INC.

FOR SUBMISSION TO

SUPPLY AND SERVICES CANADA

HULL, QUEBEC

ON

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Fabrication of FCC catalysts from Suncor Flyash Leach Residue

Final Report

for

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ORF

Fabrication of FCC Catalysts from SUncor Flyash Leach Residue
for Carbovan Inc.

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Fabrication of FCC Catalysts from Suncor Flyash Leach Residue
for Carbovan Inc.

SUMMARY

At the request of Carbovan Inc. a five phase study was initiated on the tailings produced from the decarbonation and leaching of flyash produced by Suncor Inc. The study included an initial literature search, specification analysis, physical and chemical characteristion of the residues and testing of the residue in three major applications.

The literature search revealed clearly that application of zeolites can be applied to the petrochemical , microsieve and detergent industries. There is an extremely high degree of product quality control and in nearly all major applications the products used are synthetically produced zeolites. Commercial zeolites used in the petrochemical, microsieves detergent industry are of the form Faujasite, Zeolite A, Zeolite Y or ZSM5.
The specifications of leach residues when compared to these four basic commercial zeolites are not apparently comparable.
Chemically, crystallographically and physically the residues do not appear amendable as zeolitic materials, though they are of a basic zeolite form.
With the exception of plastic filler applications, the residues do not compare favourably with presently marketed zeolite products.
Considerable effort may be required to convert the present tailings to a high value zeolite product.

1. INTRODUCTION

Carbovan Inc was formed jointly by Agra Industries Limited and Renzy Mines Limited to construct and operate a plant which can extract vanadium from waste flyash produced by Suncor Inc. at For McMurray, Alberta. Ontario Research Foundation, under the supervision of Carbovan Inc, developed an innovative process to recover vanadium and carbon from flyash. Carbovan has since obtained long term exclusive rights to obtain flyash from Suncor as well as proprietary rights to the newly developed carbon/vanadium recovery technology.

A by-product of the recovery process is a leach residue containing up tp 95% zeolite material. Preliminary test work on this by-product by Petroleum Division, Saskatchewan Research Council indicated that this material may be suitable as a fluidized catalytic cracking (FCC) catalyst. In order to have commercial value, it was considered that the physical properties and gas-oil conversion efficiency of this zeolyte type by product must be improved.

Under a cost shares program with Department of Supply and Services (DSS Serial No. 23440-7-9124/01-SQ) Carbovan Inc has evaluated the potential of Carbovan Leach Residue (zeolite) for its potential commercial application. Potential applications evaluated include: fillers, molecular sieves, detergent and FCC Catalyst Industries.

The work was divided into four major tasks.

1) A literature search regarding zeolite application.
2) Gathering of commercial zeolite specifications.
3) Physical and Chemical Characterisation of the Unmodified Leach Residue.
4) Evaluation of the Unmodified Leach Residue.

A fifth task "Modification and Apprisal of the Leach Residue" was abandoned after the results of the first four tasks revealed that this work would be superfluous.
The following report details the findings of the above four tasks.

2. LITERATURE SEARCH

2.1 Introduction

The term zeolite describes a large and expanding group of crystalline aluminosilicates whose origins lie as naturally occurring minerals but are more often found today as synthetically produced hybrids.

Zeolites are crystalline microporous solids containing cavities and channels of molecular dimensions 3A to 10 A and are often generically termed molecular sieves. Though based in alumino silicate chemistry recent developments in alumino-phosphate chemistry have expanded the compositions to include over 13 elements in addition to the more commonly know Si, Al, Ga, Ge and Fe.

Structurally the zeolites are based on an infinitely extending, three dimensional network of AlO_4 and SiO_4 tetrahedra linked by the sharing of oxygen atoms. Tens of thousands of theoretical structures are possible, while only those structures of high thermal and chemical stability have become important industrially.

Chemically the structural formula of a crystallographic unit cell of a zeolite may be expressed in terms of the oxides,

$$M_{x/n}\,[(AlO_2)_x \cdot (SiO_2)_y]_m\, H_2O$$

where M is a cation of valence N, m is the number of water molecules. The framework contains channels and interconnecting voids which are occupied by cations and water molecules. Generally the cations are mobile and can be replaced by exchange with other cations.

The molecular control of ingress and egress to reactive sites as well as the control of the size of the site itself facilitates molecular control of chemical reactions allowing significant molecular engineering of molecules usually less than 10 Å in size. As indicated before zeolites may occur naturally in the environment usually as deposits of altered volcanic ash or more significantly as synthetically produced powders. Each have their own market though despite the tremendous versatility and huge market potential, natural zeolites have yet to meet customer acceptance in most market areas. Natural zeolites have found their greatest market as dimension stone and in other areas such as water treatment, animal feed and odour control whereas synthetic zeolites have made a major impact in areas of considerably higher value particularily in catalysis, adsorbants/dessicants and detergent formulation.

2.2 NATURAL ZEOLITE APPLICATIONS (Refs 1-5)

The three major areas of application for natural zeolites are in the areas of ion exchange, water adsorption and gas adsorption. Within these three broad categories some specific applications can be identified:

Ion Exchange

- Aquaculture, removal of natural ammonia in fish farming
- Agriculture, slow release of fertilizer
- Water Treatment, Caesium removal from industrial effluent
- Radioactive waste clean up, Strontium removal from waste streams

Water Adsorption

- Dessication - localised removal of H_2O water particularly in small systems

- Heat storage/solar radiation - zeolitic high heat of adsorption allows their use

Gas Adsorption

- Odour control, ammonia fume removal associated with agriculture and pet litter

- Industrial gas, removal of impurity gases from natural gas and methane separation

Animal Feedstuffs

- Zeolites as feed supplements, considerable research has taken place in assessing the beneficial effects of including zeolites in farm animal diets.

Paper Fillers

- a small but growing market in areas where traditional paper fillers are in short supply.

The types of zeolite normally found in the natural form and which may be marketable are shown in Table 1 together with the most common applications of each of the zeolite forms.

2.3 SYNTHETIC ZEOLITES

The synthetic zeolites are high purity specialty chemicals that serve a wide range of applications. Most synthetic zeolites are thermodynamically metastable products and are prepared under closely controlled conditions. Particular attention is paid to the physical reaction environment in controlling homogenization and nucleation conditions.

The three major fields of application for synthetic zeolites are as catalysts, microsieves and as detergent builders. Table 2 denotes the major synthetic zeolite forms presently on the market.

2.3.1 Catalysts

Application in a number of fields is evident including catalyst cracking (fluid or fixed bed), hydrocracking, petrochemicals and pollution control (NO_x).

Fluid cracking catalysts provide the most important outlet for zeolites in catalysis. Crude oils are broken down into short chain or ring type hydrocarbons for refinement to the myriad of organic compounds available on the market.

An important trend in the industry is the increased production of unleaded gasoline. The demand for zeolites has consequently increased in order to improve the octane content during gasoline production.

2.3.2 Microsieves Applications

The major application of molecular sieves is as dessicant in a combination with silica gel and alumina for the removal of water, hydrocarbons or other fluids. Though commonly used in window sealants and automotive brake systems for removal of condensation vapours, industrial gas drying accounts for the large majority of molecular sieve use. Removal of water from natural gas after well tapping, ethane gas dessication and jet fuel drying are high volume zeolite users.

Gas streams may also be treated with molecular sieves for CO_2, H_2S and carboxyl sulphide removal while more exotic organic gases can be selectively removed by choosing appropriate zeolite species whose polarity and molecular porosity are specifically designed for such purposes.

2.3.3 Detergent Builders

In response to environmental pressures concerning phosphate build up in the environment; STPP (sodium tripolyphosphate), used to bind calcium and magnesium ions in wash water before interference with the dirt removing surfactants in detergents, has been substituted by zeolites.

Some zeolites have a particular affinity for calcium and magnesium ions in water by exchange with sodium. The released sodium ions remain in solution and do not precipitate on to the fabric. Other advantages other than cost effectiveness of zeolites are buffering action in pH adjustment during washing, the ability for zeolites to absorb dyes released during the wash cycle and the strong surfactant adsorption characteristics of the zeolite allowing an overall increase in the total surfactant available.

2.3.4 The Market Place

The largest area in the consumption of zeolite is in detergents, with 80-90% of worldwide sales to this application. The U.S. market however is not as high as this due to recent reductions of zeolite in detergent formulations in favor of alternative chemistry. The second largest market is in catalyst products for petrochemicals representing 10-15% of the market (higher in the U.S. due to a wider petrochemical industrial base.) Finally some 5-10% of total zeolite production is in adsorbant applications.

In the sections to follow a somewhat more detailed assessment of zeolite applications will be made together with some specifications of the most commonly found zeolites and their applications. Where figures are available specific tonnages will be quoted as well as assessment of the market share of those particular zeolites.

2.4 ZEOLITE AS CATALYST (Refs 5-24)

Zeolite based catalysts find application in a number of fields including catalyst cracking (fluid or fixed bed), hydrocracking petrochemicals and pollution control. Four major mechanisms explain zeolite activity.

1. Hydroxyl groups in the zeolite framework release hydrogen ions to the reactant.

2. The inherent electrostatic field of the zeolite rearranges the atomic bands of the reactant.

3. Metallic cations in the zeolite structure have an effect.

4. Holes in the framework of the zeolite, caused by missing oxygen atoms produce a net positive charge in the region of the reaction.

These characteristics cause the carbon linkages in some hydrocarbons to be altered while others remain unaffected. Similarly certain molecules are selectively excluded from reactions by being too large to pass through zeolite pores.

The major commercial zeolites and the cracking processes to which they have been adapted are listed in Table 3.

2.4.1 Fluid Catalyst Cracking (FCC)

The manufacture of zeolite catalysts for petroleum refining is a $700 m/annum business worldwide with an approximate 5% per year growth.

In the FCC process heavy petroleum fractions are converted to lighter boiling gasoline and light fuel oils. Liquefied petroleum gas (LPG) fuel gas, heavy fuel oil and petroleum coke are the major by products. FCC processes optimise high octane gasoline production in order to minimize the production of the above by-products.

Zeolite X (rare earth doped Faujasite) had been the initial catalyst in gasoline production, but has been superseded today by zeolite Y which has a higher SiO_2/Al_2O_3 ratio and offering better catalytic properties. Higher silica faujasite zeolites are now coming on the market due to improvements in synthetic process technology. Again the advantage of these products is to increase the SiO_2/Al_2O_3 ratio and decrease the acid site density, i.e. the number of exchange points required to maintain electrical neutrality in the structure. This makes for a more selective catalyst during cracking and specifically the production of high octane olefins with reduced product cracking and hydrogen transfer. The incorporation of ZSM-5 catalyst to selectively convert low octane paraffins to high octane components is not uncommon.

2.4.2 Hydrocracking

The second largest application for zeolites involves hydrocarbon cracking under high hydrogen partial pressures whereby hydrogen is added to the final product. Processes take place at elevated temperatures and pressures. The large pore zeolites X, Y and mordenite are favored due to their long life, up to six years, and rejection of contaminants such as sulphur and nitrogen. High silica faujasites are preferred where heavy oil feeds are used.

2.4.3 Isomerisation and Selective Cracking

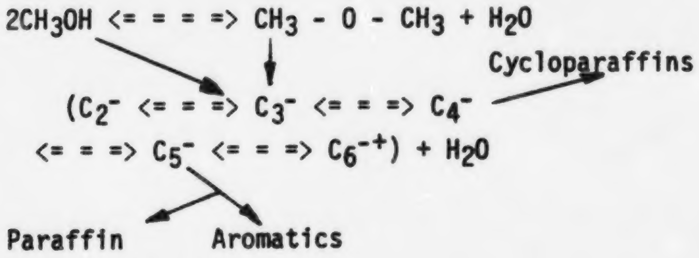
Due to the increased octane requirements in gasoline caused by the removal of tetraethyl lead considerable effort has been made to improve pentane and hexane isomerisation capacity in refineries. Typically mordenite type zeolite with a Pt inclusion is used for the isomerisation. Some 20% of all refinery capital expenditures were made on installing or upgrading this system in the past four years.

Liquified petroleum gas production from pentane and hexane by catalyis is known as selectoforming. Reactions take place at high temperature and pressures with high H_2/hydrocarbon mole ratios. Erionite type zeolites were originally used but improvements on the process for direct conversion of paraffin to high octane gasoline with ZSM-5 zeolite was developed by Mobil in the mid 70's. Two other important selective forming processes are conversion of light hydrocarbons to monocyclic aromatics (high temperature process) and olefins to gasoline and distillates, (low temperature processing). In both cases ZSM-5 zeolite is used as catalyst. In the former process the medium sized pore inhibits coke formation and in the latter, the shape selectivity of the zeolite allows production of high quality jet fuels.

2.4.4 Synfuels Production

(1) Methanol to Gasoline

The conversion of natural gas directly to liquid fuels (MTG process) has been the most interesting development in recent years regarding zeolite catalysts. The potential of the process has generated the installation of one operating plant in New Zealand. The reaction pathway is


2CH3OH <= = = => CH3 - O - CH3 + H2O
Cycloparaffins
(C2- <= = => C3- <= = => C4-
<= = => C5- <= = => C6-+) + H2O
Paraffin
Aromatics

ZSM-5 zeolite is critical to the process due to its medium pore size. Smaller pores produce no aromatics while larger pore zeolites deactivate rapidly.

2. Ethanol to Gasoline

The production of gasoline from fermentation products has been investigated using ZSM-5 zeolite. The reactions and the process is similar to methanol conversion with the advantage that dilute ethanol (i.e. fermentation products containing high volumes of H_2O) may be considered as adequate starting material.

3. Fischer-Tropsch/Zeolite Process

Conversion of synthetic CO + H_2 to liquid hydrocarbons has been known for half a century. However, the process is singularly expensive in comparison to ground sources of crude oil.

The F-T product usually is in the form of straight chain paraffin and olefins. These are readily converted by ZSM-5 catalytic processing to gasoline as previously described. At present only South African interests have pursued industrial development.

2.4.5 Other Petrochemical Processes

Many other minor petrochemical processes utilize zeolites for particular conversion processes. The following represents a list of processes and the zeolite catalyst employed.

Toluene Disproportionation	-	Zeolite X/ZSM-5
Etylhezine synthesis	-	ZSM-5
Methanol to Olefins	-	ZSM-5, SAPO Linde
Toluene Alkylation	-	Faujasite, ZSM-5
Para selective processing (Toluene, styrene)	-	ZSM-5
Xylene isomerisation	-	ZSM-5
Distillate Dewaxing	-	ZSM-5, Mordenite

In all the above cases the zeolites are modified with the addition of Pt/Pd or rare earth cations in proprietary processes.

2.4.6 NO_x Gas Treatment

Future conversion of noxious NO_x gas to N_2 from a variety of industrial sources is likely to include zeolite catalyst processing to a greater degree. Mordenite, and/or Y zeolites have already been proven in the reaction mechanism in promoting ammonaical conversion of NO_2 and NO to nitrogen. The application of this process is already being made to new European power plants where flue gas emissions are closely controlled. It is likely that this will be a high growth area zeolite application.

2.4.7 The Market

Two major trends in the marketing of cracking catalysts are now prevalent. Firstly, though the largest market (FCC) is now maturing a 3-5% annual growth is now predicted for the next 2-3 years. Little growth is seen however in the hydrocracking catalyst market as the incentive to process heavy crudes diminishes as the price difference between light and heavy crudes diminishes. Less demand for the hydrocracking catalysts will consequently result.

The second major trend is the increased production of high octane gasoline. This has resulted in increased demand and research into producing Y type zeolites. In particular, interest in producing stable, tangible catalysts has been prevalent rather than further enhancing the already exceptional catalytic properties of these types of zeolites.

Though there is overcapacity in the western markets, causing lively competition particularly for FCC zeolites, the market is generally stable. Producers are now promoting more specialized "value added" types of materials in new technology areas such as synfuels and NO_x abatement systems. The next bulk market to develop will likely be in South America where residual cracking is more commonplace and higher catalyst volumes required.

As a general comment the large majority of catalysts developed for the petrochemical industry are manufactured under strictly controlled process parameters. Raw materials are either synthetically produced high purity products or at the very least, they are naturally occurring mineral phases which have been pretreated to remove any non beneficial impurities. The competition, particularly for the FCC catalyst market appears to have stabilised.

2.5. MICROSIEVES

2.5.1 General Applications

As described in the introduction, zeolites, because of their microporous crystalline nature, are well suited to application as molecular adsorbants. The zeolites have the ability to be highly selective, have high adsorption capacity and have good stability particularly during regeneration.

The properties of the three major types of zeolites are given in Table 6. These materials account for 90% of the adsorbant market. In large part the performance of each adsorbant is dependent on the size of the molecular pores existing in each of the unit cell structures.

The selectivity of the adsorbants is consequently delineated largely by this pore size. Some degree of flexibility in the structure is permitted by ion exchange modification of the basic unit cell. This allows some tailoring of the pore sizes to suit certain applications. Highly selective adsorbants may be manufactured by careful adjustment of the polar properties as well as the final pore size of the zeolite.

The equilibrium selectivity of zeolites is determined by two major factors.

(i) The Van der Walls forces acting on the sorbate surface

(ii) The degree of polarity at the sorbant surface

Van der Walls forces tend only to be significant on homogeneous non polar surfaces (high silica zeolites). The effect is proportional to the size of the adsorbed molecules.

Due to the presence in zeolites of exchangeable cat-ions, polar molecules such as H_2O, N_2, CO_2 have a higher affinity for adsorption than non polar species. The affinity increases with cation charge and decreasing cation radius.

Examples of these former effects can be seen in the sorption of u-hexane from benzene, where the n-hexane molecule is precisely the right "fit" for the ZSM-5 structure. Because of the close fitting nature the Van der Walls interaction energy will be at a maximum. In the latter, the selectivity affects the affinity for unsaturated hydrocarbons over paraffin by zeolites of high silica/alumina ratio. There is a direct relationship to the change in polar strength of the adsorbant with microsieve selectivity.

The adsorption process itself is dependent on three major factors:

(a) The phase of the operation itself (gas or liquid)

(b) The method by which the adsorbent is regenerated.

(c) The contacting scheme.

In (a) low temperature gas phases are favored over high temperature liquid separations due to obvious savings in energy consumption. In (b) four regeneration methods are common:

(1) Pressure modulation

(2) Temperature shifting

(3) Displacement by competitive adsorption

(4) Inert purging

2.5.2 Separation and Purifying Systems

Tables 7 and 8 indicate the majority of systems presently involving zeolitic microsieves. Essentially there may be generically split into hydrocarbon separation, carbohydrate treatments and air separation.

Hydrocarbon separations are in large part based on the production of linear paraffins from a variety of feed sources. The linear paraffin produced (or extracted) are used in synthetic detergent production while the branched and cyclic isomer produced as raffinate enter high octane gasoline or jet fuel production system. Aromatic separations though difficult by conventional distillation methods are made possible by the use of selective adsorption processes (Table 7).

Carbohydrate separations are generally limited to the food industry where the production of fructose-glucose mixtures has been made from natural carbohydrate food materials. A two phase operation is common whereby initial fructose/glucose separation is made (fructose as raffinate) and the glucose containing saccharides is further treated to adsorb glucose only. The selection of adsorbant is critical and zeolites compete with ion exchange resins that depend on the choice of process.

The production of O_2 directly from air separation systems is as yet not a "bulk" system - cryoganic processes presently being preferred. Small scale operations are relatively common, 5A or 13X zeolite being the N_2 adsorbing element.

2.5.3 The Market Place

In the zeolite market microsieve grade zeolites used in adsorbent and dessicant applications consume approximately 10% of total zeolite production. Table 9 indicates approximate worldwide tonnage use of microsieves. The market has indeed been growing at around 5%/annum and is predicted to do so through the early nineties. However, production has easily met the demand as a large majority of the catalyst producers are strongly associated with this market.

While synthetic zeolite producers argue that it is impossible to control product purity and hence the properties of natural zeolites, it is often natural minerals that are the feed stock to synthetic zeolite processing. Microsieve manufacturers tend to follow this view particularly in the area of specialized processing where production and in particular precise control of the final zeolite product is critical to the process to which the zeolite has been developed.

2.6. DETERGENT APPLICATIONS (REFS. 37-43)

2.6.1 General

The conventional water softeners used in detergent powder and cakes are orthophosphate, pyrophosphatic and mainly sodium tripolyphosphate (STPP). However, STPP being entroropic when incorporated into detergents poses serious environmental problems. It promotes rapid development of algae which are hazardous for water fauna and fouls effluent treatment plants.

Zeolite with inherent ability to exchange mobile Na+ and K+ cations allows water hardness to be reduced with adsorption of Ca+ and Mg+ cations. In the correct formulation close to 99% removal of the dissolved calcium and magnesium is possible.

Table 10 indicates the approximate total world zeolite usage in the detergent industry for 1986. Clearly these enormous tonnages demonstrate the effect on the detergent industry of the legislation banning STPP coming into effect. In all cases synthetic Zeolite A, or a proprietary variation of this zeolite is the product incorporated into the detergent formulation.

The advantages of this zeolite may be summarized:

(i) It can be incorporated directly into detergent compositions due to its fine particle size and is effectively washed out during rinsing.

(ii) Provides excellent combination of high ion exchange capacity with high binding power for metallic ion present in hard water.

(iii) Does not cake during storage as does STPP.

(iv) It has a high moisture holding capacity reducing sticking during formulation.

(v) It is cheaper than STPP.

(vi) Is an odourless free flowing white powder.

Natural zeolites are not suited for detergency applications since their particle size is not optimal and the presence of heavy metal ions is detrimental in view of the possible catalytic action in the decomposition of other components of the detergent. Synthetic zeolite A satisfies the requirements for detergency application in particular as to particle size, purity, core exchange capacity and rate. Less than 200 ppm metal ion impurities can be tolerated. Transformation of mineral zeolites in the production of zeolite A may satisfy the above requirements providing, in particular, that metal impurities are kept below the approximately 200 ppm level and that the final product meets all other specifications.

2.6.2 Adsorption Process

Zeolite A removes hardness ions by ion exchange rather than by chelation which is associated with STPP. Most of the ion exchange capacity of Zeolite 4A exists within 11.4 angstrom cavities which are reached through 4.2 angstrom pore openings. The pores permit passage of Ca ions into the cavities where they exchange for Na ions. Magnesium ions have an effective ionic radius greater than 4.2 Angstrom, and do not pass as easily. This factor requires that zeolites may be used in conjunction with STPP (where permitted) or with non phosphate compounds and some reformulation in order to assist in Mg ion uptake.

2.6.3 Market Place

In the three major world zeolite markets growth potential is seen to the early 1990's.

In Europe, the market is expected to exceed 500,000 tpa, assuming, as has been indicated that most countries ban the use of STPP. Major producers are all presently expanding detergent zeolite production with the majority being in synthetic zeolite A forms. The Japanese market is estimated at 150,000 tpa for 1990. As in Europe the demand is expected to increase due to STPP legislation. As yet only a voluntary ban on STPP has been implemented by the detergent companies. All zeolite supplied to the Japanese market is locally produced and at this date, as in Europe, there is an oversupply of zeolite A. The U.S. market is somewhat less predictable due to the fact that only 25% of U.S. states have banned STPP and that one major consumer of detergent zeolite, Proctor and Gamble, having initiated zeolite usage, now excludes it due to reformulation using alternative chemicals. Present tonnage runs at 70,000 tpa, though the market is expected to increase significantly due to the highly competitive price of zeolite A compared to alternative water softening formulas.

2.7 FILLER APPLICATIONS (REFS. 32-36)

The use of zeolite in filler/extender applications is presently extremely limited. Normal filler applications include the following major areas:

1. Plastics
2. Cements
3. Papers

2.7.1 Plastics

With the exception of unproven novel applications there are no applications using zeolites as fillers. Though the intrinsic physical properties of zeolites bind them to inclusion in plastic compounding there appears to be no cost advantage over present fillers on the market. These would include calcium carbonate, kaolin and other natural stone extenders.

The application for zeolites according to the patents presently being listed would likely be in areas where their unique properties are as "value added" materials. Typical areas over which some interest has been taken is in the production of solid polyurethane foams. During the reaction between isocyanate and polyol the presence of water reacts with further isocyanate to give off carbon dioxide. This blowing action is highly desirable in the production of forms but not so where a homogeneous solid is desired. The addition of a suitable zeolite in the formulation causes uptake of the water to the zeolite during the initial polymerization with the result that secondary CO_2 production is inhibited. Indeed the zeolite may adsorb any other low molecular mass compound which may be felt to be deliterious to the desired product.

As yet this application has been proven with only "pure" zeolite additions and is extremely limited to a single process.

A second example of plastic filler application is in the production of high mineral phase sheets. The surface of the sheet is treated with zeolite mineral or with other mineral fillers in order to improve the final properties of the fibre sheet. Again no production details are available and the application extremely limited.

The use of "loaded" zeolites has been proposed as an application in the production of solid air deodorants. Porous zeolite is treated with a deodorant molecule. The zeolite is then bound in a "porous" plastic case, and the deodorant then decays to atmosphere with time.

A similar technique has been proposed in conjunction with the hardening of dental fillings. Zeolites could be used as carrier for hardening catalysts in dental formulations based either on metal or organic matrices. The release of the catalyst over a short period of time allows hardening of the filling matrix after a suitable moulding time.

It is clear that bulk filler applications have yet to be formulated using zeolite in the plastics field. An appraisal of the literature tends to reveal that any future applications will likely involve pure synthetic zeolites or high purity natural zeolite forms. The applications themselves will be novel, low volume zeolite products.

2.7.2 Cements

The application of zeolite as cement filler is generally conceded to be relatively limited at the present time. The application of flyash in concrete, however, is well documented particularly in the field of alkali aggregate reactivity suppression. Excess metal alkalis are preferentially combined before reacting with silicate bearing aggregate. It would appear likely that zeolitic flyash may provide some interest in this area.

One area of application receiving considerable interest is the production of high early strength concrete utilising limestone and zeolite as fine powder. Though the zeolite essentially behaves as a ground slag or flyash in promoting long term strength it particularly provides high sulfate resistance and low heat of hydration during curing. These advantages must be balanced against the high water requirement usually present in the zeolite cement and the low early strengths usually observe during curing.

The performance of a particular zeolite depends greatly on the individual properties of that zeolite. In countries where pozzolan additions to cement formulas are highly desirable, i.e. where clinker production costs are to be minimized, the use of zeolite in cement formulation is common, e.g. China, Russia, etc. Natural zeolites commonly used are usually mordenite or clinoptilite. In North America zeolite utilization is limited but not unknown. The formulation, type of zeolite and application is usually proprietary and detailed information difficult to acquire.

2.7.3 Paper Filler

In areas where natural paper fillers are not prevalent attempts have been made to incorporate natural zeolites as paper fillers. Notably in Japan, the Zeiklite manufacturer company utilizes a bleached clinoptilolite (natural zeolite) in paper manufacturing. The company produces some 50-60,000 tpa of the white zeolite exclusively for the paper industry.

Clearly any application in the pulp and paper industry requires that the zeolite compete with more traditional fillers such as kaolin both in price and in quality. Due to plentiful kaolin resources in the North American market this application has not been investigated seriously.

2.8 NEW TECHNOLOGY AND TRENDS IN THE TRADITIONAL ZEOLITE MARKETS (REFS. 44-49)

2.8.1 New Technology

With 1000 patent applications/per annum associated with zeolite technology, the development of both unique processes as well as new zeolite hybrids is overwhelming.

Within the petrochemical industry continued development of the ZSM-5 catalyst particularly for FCC catalysts is prevalent. The major interest appears in extending substitution of elements such as Ga, Ge, B, Fe and Be into the framework allowing modification of acid strength and improved catalytic properties. Crystalline metal alumino phosphate zeolites discovered recently have unique structures including larger pore sizes than faujasite, while faujasite itself is under constant study in improving the Si/Al ratio for more selective hydrocracking processes.

The separation of catalyst applications from microsieve applications is continuously becoming less clear as innovations in both areas in the creation of new zeolitic materials almost compete with each other.

2.8.2 Fly Ash Treatment

In the synthesis of zeolites further attention is now being paid to natural sources of zeolitic materials. Methods of activating or "regenerating" these materials are becoming more prevalent , however extreme limitations on natural zeolites are inevitable due to the natural impurities present.

In Europe some initial studies have been made into the direct conversion of fly ash to consumable forms of zeolite. Specifically the formation of faujasite and phillipsite has been documented. The proposed systems incorporate enclosed treatment of fly ash with NaOH with long reaction times (40 days). The performance of these materials, particularly in regards to FCC applications has not been assessed. The production of Zeolite A from fly ash has also been attempted with some success with very short reaction times. In both the above examples complete transformation of the alumino silicate phases in the fly ash was not achieved with best results in the 50% conversion range. The Na/Al/Si ratios must be closely monitored for the correct transformation to take place. The projected uses for these new materials would be in "one-way" adsorption processes, i.e. where no regeneration is contemplated.

3.0 COMMERCIAL ZEOLITE SPECIFICATIONS

In Tables 11-14 and Appendix I the manufacturers' specifications are listed for those zeolite products applied to the four areas of application presently under consideration in this report. In the case of plastic filler applications, examples of typical mineral fillers used are given together with their properties.

4.0 PHYSICAL AND CHEMICAL CHARACTERISATION OF UNMODIFIED LEACH TAILINGS

In table 16, 17 and 18 (XRD reports) information is provided as to the chemical and physical content of the analysed leach tailings. Data reported here concerns three materials.

(a) Flotation tails from a decarbonizing flotation whose feed was a blend of 3:1 ESP/BH flyash.

(b) Tailings produced from leaching (a) in 150 Kg/tonne NaOH at 200°C for 1 hour (NaOH leach).

(c) Tailings produced from leaching (a) in 150 Kg/tonne NaOH + 325 Kg/tonne Na_2CO_3 at 200°C for 1 hour (Na_2CO_3 leach).

These materials were all thoroughly washed and oven dried at 110°C prior to blending and sampling for parameter measurement.

In addition a sample of ESP only flotation tail leached as in (c) above was also characterised by XRD methods. (Table 18).

4.1 Physical Characterisation

Results presented in Table 16 reflecting parameters determined from N_2BET measurements are those found by Micrometrics Georgia (Progress Report 4, Appendix V)

These results are felt to be more accurate as some questions as to ORF instrument accuracy in results given in Progress Report 1 and 2 were noted by ORF operators.

Porosity measurements concerning pore size data clearly reveal the "macro" porosity of the materials. Though the material is zeolite in nature the expected molecular pore size of 4-5A is not measured. SEM work by Western University (reported separately to Carbovan) showed the high degree of fractured and "porous" ash particles at particle sizes <1ppm. This macroporosity clearly interferes with physical molecular pore size measurements.

4.2 X Ray Diffraction

The XRD patterns, Table 18, shows the analcime phase to be clearly dominant in any of the leach tailings tested. An additional XRD pattern of ESP flyash, caustic/soda ash leach tailings of ESP flyash, clearly reveals the almost exclusive presence of anaclime zeolite. This concurs with the previous X-ray diffraction patterns of leach tailings whose source included BHA flyash.

4.3 Chemical Analysis

Chemical analysis of the leach feed and tailings clearly shows the high metal ion content of the materials under consideration, together with the high level of trace metals present.

A comparison of the manufacturers specifications and the measured properties of leach residue shows apparent discrepancies, not least of which is the form of the zeolite produced during leaching.

5.0 UNMODIFIED LEACH TESTING

All samples made available for unmodified leach testing were prepared in batch form and split samples sent for testing. The following represents the list of materials prepared by ORF for each of the four applications studied.

1) FCC applications (samples tested and reported to Carbovan by SRC)

Sample E58 - 3:1 ESP/BHA float tails -- caustic leach tails
E59 - 3:1 ESP/BHA float tail -- caustic/carbonate leach tail
E60 - 3:1 ESP/BHA float tail --
E69 - ESP float tail -- caustic/carbonate leach tail
E70 - E69 + Al_2O_3 (20%)
E77 - ESP float tail - caustic leach tail

2) Microsieve Application, Detergent Applications, Filler Applications

E63 - 3:1 ESP/BHA float tails -- caustic leach tail

In each of the samples above (with exception of E70), leach on flotation tailings were dried at 110°C prior to packaging and subsequent testing.

Reports regarding the performance of leach tailings in the three applications, Microsieve, Detergent and Filler are given in Appendicies II, III and IV. Reports were submitted to ORF Minerals Resources group by

Appen. II	Nova Husky Research ---	Microsieve Application
Appen. III	ORF Plastics Division ---	Filler Application
Appen. IV	ORF Minerals Division ---	Detergent Application

Materials preparation and identification for each system tested include SRC materials tested. (as listed in SRC report)

The conclusions of these reports reveal clearly that there is no immediate application of this material with the exception of plastic fillers. Here the material is no better or worse than those fillers presently on the market. For filler applications, modification to the material is recommedned in order to take advantage of the basic zeolitic properties present. This may allow added value to be built into the material for specific applications. It would appear that not inconsiderable development work would be required to achieve this.

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Previous Work Review

Initial results in testing leach residues for catalytic activity indicated that from gas-oil conversion tests the leach residues, when diluted with sand for improved rheological properties, approached conversion rates found for commercial grade catalysts. Further testwork was consequently approved and results reported as follows.

6.2 Literature Survey and Specification Analysis

From the extensive literature survey major zeolite applications were found to apply in three major areas.

- petrochemical industry in fluid cracking catalyst application
- microsieve application in the treatment of liquid and gas stream
- detergent applications in replacing STPP

With respect to the petrochemical industry and microsieve technology an extremely wide range of zeolite types and applications is prevalent. A common denominator to all applications is the close control over product quality.

The zeolite sources are all synthetic in nature, though feed materials to the zeolite production process may have natural mineral origins.

In general, the zeolite market is expanding, though changes particularly in petrochemical processing may change the types of zeolite that will be utilised in the future. By far the largest tonnages of zeolite are associated with the detergent market. The market is limited to very specific zeolite types of extremely high purity.

No major application in the fillers/extenders area was indentified. Recent work has shown the treatment of flyash in caustic solutions can produce well crystalline zeolitic forms from a variety of processing routes.

6.3 Specification Analysis

The following represents a summary of the critical parameters found in each of the technologies applied to zeolites.

FCC Applications

Type:	Faujasite, Linde X, Linde Y
Area:	300 m^2/g
Particle Size:	60 um
Catalytic Activity:	75% (at equilibrium)
Iron:	3700 ppm (at equilibrium)

Microsieve Application

Type:	Faujasite, Zeolite A, Zeolite Y
Pore diameter:	3.0A - 8.0A

Synthetic High Purity Products

Detergent Applications

Type:	Zeolite A (85%) Sodalite (0-15%)
Size:	4 um
Calcium Entry Capacity:	255 mg ($CaCO_3$)/gram minimum
Color:	White
Metal Ion Content	<200 ppm

Filler Application (Calcium Carbonate)

Type:	Calcium Carbonate
Color:	White
Particle Size:	3.5 um (Grade I)
Oil Adsorption:	21.5 (ASTM D281)
Surface Area:	3.26 m^2/g

6.4 Physical and Chemical Parameters of Leach Tail (Caustic)

The summary of parameters below includes those which are pertinent to the specifications summarized in 6.3 above.

Mean Particle Size:	15 um (optical analysis)
Surface Area:	59.3 m^2/g
Porosity:	75%

Oil Adsorption:	57.7 (ASTM D281)
XRD:	Largely Analcime zeolite and unreacted mullite.
Chemical:	High metal ion content ($Fe_2O_3 > 9\%$, $TiO_2 > 3\%$)

Measurements indicate that physically the material does not presently conform to any of the zeolite applications considered. Specifically particle size, porosity and pore deminsions do not conform to commercial zeolites in any application.

Chemically and crystollographically the material is presently not in any zeolitic form which is found in any of the applications under consideration. Specifically the high metal ion content interferes with zeolite properties and the analcime form is itself not amendable to catalytic, filler or adsorption proccesses.

6.5 Unmodified Leach Residue Testing

6.5.1 Microseive Testing

Testing of 3:1 ESP/BHA leach tailings for microseive activity in the adsorption and desorption of H_2O clearly indicated the material would have no commercial value in the adsorption of most non-polar and polar components.

Results showed that the tailings had a capacity of ten times less than that of a commercial 13X microsieve.

6.5.2 Detergent Testing

Basic studies in the adsorption of calcium and magnesium ions from water solutions showed almost zero uptake of either ion. Physically and chemically the tailings also do not meet detergent zeolite specifications.

6.5.3 Filler Testing

From the extensive tests involving compounding of the leach tails with polyurethane several conclusions can be drawn. The behaviour of 30% filled polypropylene is as expected for any approximately spherical filler. The observed outgassing indicates possible applications as liquid carrier filler and further investigation has been recommended.

6.6 RECOMMENDATIONS

From the above conclusions it is clear that further work would be required to seriously change the chemical and crystallographic nature of either flotation tails or leach tails, produced from both of the leach systems under test, to allow production of a true zeolite.

Filler applications for the material appear to be one natural area where use could be made of this material though some development study would be required.
The pozzolanic nature of the material should be reviewed in order to assess the possible application for cement replacement in concrete.

Chemical alteration of flyash by pug leaching in caustic solutions has been reported in the literature as a possible crystal altering system. Careful control of the Si:Al:Na ratio may provide a processing route for FCC type catalyst production.

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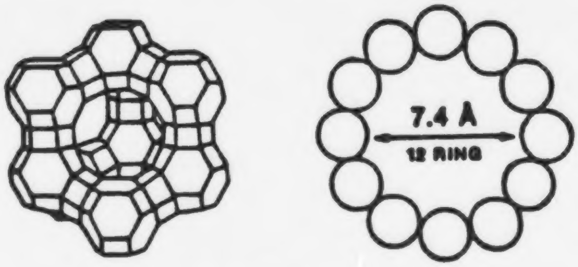
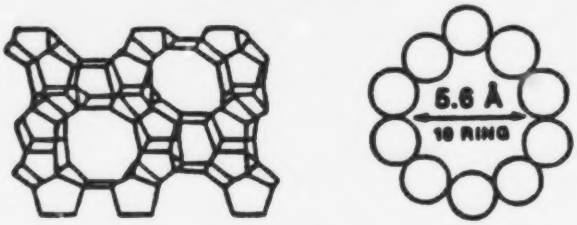
7.0 TABLES & FIGURES

Figure I

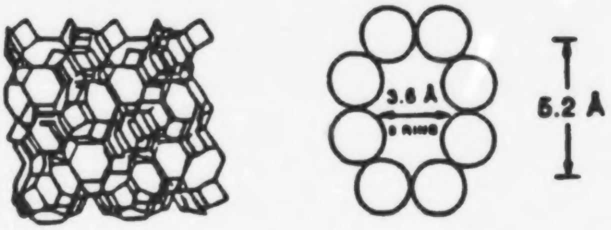
Framework Structures of Major Zeolites



Y ZEOLITE



ZSM-5


3.6 Å
8 RING
5.2 Å

ERIONITE

TABLE 1

IMPORTANT ZEOLITES (Ref 4)

	Typical unit-cell content	Void Volume (%)	SG	Ion-exchange capacity mequiv/g
Group 1: Single 4-ring (S4R)				
Analcime	$Na_{16}[(AlO_2)_{16}SiO_2)_{32}].16H_2O$	18	2.24-2.29	4.54
Phillipsite	$(K,Na)_{10}[(AlO_2)(SiO_2)_{22}].20H_2O$	31	2.15-2.20	3.87
Laumonite	$CA_4[(AlO_2)_8(SiO_2)_{46}].16H_2O$	34	2.20-2.30	4.25
Group 2: Single 6-ring (S6R)				
Erionite	$(Ca,Mg,K_2,Na_2)_{4.5}[(AlO_2)_9(SiO_2)_{27}].27H_2O$	35	2.02-2.08	3.12
Group 3: Double 4-ring (D4R)				
A (Linde)	$Na_{12}([AlO_2)_{12}(SiO_2)_{12}].27H_2O$	47	1.99	5.48
Group 4: Double 6-ring (D6R)				
Chabazite	$(Ca_2[(AlO_2)_4(SiO_2O_8].13H_2O$	47	2.05-2.10	3.81
Group 5: Complex 4-1, T_5O_{10} unit (T_5O_{10})				
Natrolte	$Na_{16}[(AlO_2)_{16}(SiO_2)_{24}].16H_2O$	23	2.20-2.26	5.26
Group 6: Complex 5-1, T_8O_{16} unit (T_8O_{16})				
Mordenite	$Na_8[(AlO_2)_8(SiO_2)_{40}].24H_2O$	28	2.12-2.15	2.29
Group 7: Complex 4-4-1, $T_{10}O_{20}$ unit ($T_{10}O_{20}$)				
Clinoptilolite	$Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$	34	2.16	2.54

TABLE 2

COMMERCIALLY AVAILABLE ZEOLITES (Ref 8)

Zeolite	Pore Size (A)	Composition Si/Al	Cation
Faujasite			
X	7.4A	1-1.5	Na
Y	7.4	1.5-3	Na
US-Y	7.4	>3	H
A	3	1.0	K,Na
A	4	1.0	Na
A	4.5	1.0	Ca,Na
Chabazite	4	4	"N"
Clinoptilolite	4x5	5.5	"N"
Erionite	3.8	4	"N"
Ferrierite	5.5x4.8	5-10	H
L type	6	3-3.5	Na,H
Mazzite	5.8	3.4	Na,H
Mordenite	6x7	5.5	"N"
Mordenite	6x7	5-6	Na
Mordenite	6x7	5-10	H
Offretite	5.8	4	K,H
Phillipsite	3	2	"N"
Silicalite	5.5		H
ZSM-5	5.5	10-500	H

TABLE 3

MAJOR COMMERICAL CATALYTIC ZEOLITE PROCESSES. (Ref 8)

Process	Zeolite	Products
Catalytic cracking	faujasite	gasoline, fuel oil
Hydrocracking	faujasite	kerosene, jet fuel benzene, toluene, xylene
Hydroisomerisation	mordenite	i-hexane, heptane (octane enhancer)
iso/n-paraffin separation	Ca-A	pure n-paraffins
Dewaxing	ZSM-5 mordenite	low pour point lubes
Olefin drying	K-A	polyolefin feed
Benzene alkylation	ZSM-5	styrene
Xylene isomerisation	ZSM-5	paraxylene

TABLE 4

COMMERCIALLY IMPORTANT ZEOLITES USED IN CATALYTIC APPLICATIONS (Ref 13)

Zeolite	Pore Size (A)
Large Pore	
Faujasite (Linde type X and Linde type Y)	7.4
Mordenite	2.9 x 5.7 6.7 x 7.0
L TYPE	7.1, 1D
Medium Pore	
ZSM-5	5.4 x 5.6 5.1 x 5.6
Synthetic	3.4 x 4.8
Ferrierite	4.3 x 5.5
Small Pore	
Erionite	3.6 x 5.2

TABLE 5

WORLD CATALYST CONSUMPTION (Ref 4)
(estimated metric tonnes)

	U.S.	Europe	Other
Catalytic Cracking	165,000	50,000	85,000
Hydrocracking	1,300	300	1,100
Others	600	300	200
Synfuels	---	---	100
Petrochemicals	<200	<200	<100
NOx Reduction		<200	<300

TABLE 6

STRUCTURAL DETAILS OF IMPORTANT ADSORBENTS (Ref 11)

	Zeolite A*			Faujasite*	
	3A	4A	5A	Zeolite X	Zeolite Y
Unit Cell Contents*	$K_{12}[AlO_2-SiO_2]_{12}$	$Na_{12}(AlO_2-SiO_2]_{12}$	$Ca_6[AlO_2-SiO_2]_{12}$	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}]$	$Na_{56}[(AlO_2)_{54}(SiO_2)_{136}]$
Demensions	--	Cubic: 12.3A	--	Cubic: 12.5A	Cubic: 12.35A
Si/Al	--	0.9-1.0	--	1.0-1.5 (higher in dealum forms)	
Framework Density ($g\ cm^{-3}$)	--	1.27	--	1.31	1.25-1.29
Crystal Density ($g\ cm^{-3}$)	1.69	1.52	1.48	1.54	-1.42
Pore diameter (A)	3.0	3.8	4.3	8.1+	8.1
Largest Molecules	H_2H_2	C_2H_6Xe	CF_4 n-paraffins	$(C_4H_2)_3N$, dimethyl naphthalenes	

* Dehydrated
** Pseudo Cell
*** Ideal value including sodalite cages

+ Reduced somewhat in Ca** form

TABLE 6 cont'd

STRUCTURAL DETAILS OF IMPORTANT ADSORBENTS

	Pentasil** Silicalite/ZSM-5
Unit Cells Contents*	$(SiO_2)Na_n(SiO_2)_{96}$ $(AlO_2)(96-n)$
Demensions	20.1A* Orthorhombic 19.9A** 13.4A***
Si/Al	- 10 1.76
Framework Density $(g\ cm^{-3})$	1.76
Crystal Density $(g\ cm^{-3})$	cylindrical in perpendicular direction 5.4 x 5.6 and 5.1 x 5.5
Largest Molecules	CCl_4 m-axylene

TABLE 7

PURIFICATION PROCESS WITH ZEOLITE ADSORBENTS (Ref 29, 30)

	Feed	G/L*	Adsorbent
Drying of	- natural gas	G	4A
	- air	G	4A
	- refrigerants (chlorocarbons)	G/L	modified 4A
	- cracked gas	G	3A
	- organic solvents	L	3A
	- acid gas	G	chabazite
CO_2 removal	- from air in submarines/ spacecraft	G	4A
H_2S removal	- from sour gas	G	CaA or Ca chabazite
SO_x9NO_x removal (Purasiv)	- from air	G	silicalite
Kr^{85} removal	- from air	G	silicalite or de-alum H-mordenite
I^{129} removal	- from air	G	AgX, Ag mordenite
Concentration of alcohols	- from dilute aqueous alcohol	L	3A, 4A

* Gas or Liquid

TABLE 8

BULK SEPARATION USING ZEOLITE ADSORBENTS (Ref 29, 30)

	Process	Feed	G/L*	Adsorbent
Linear Paraffin Separation	Isoslv	C_6-C_{10} Distillate	G	5A
	BP		G	5A
	TSF	C_{10}-C_{16} Kerosene	G	5A
	Ensorb	C_{10}-C_{16} Kerosene	G	5A
	Elf-N-Iself	Light Naphtha	G	5A
	Molex	Kerosene	L	5A
Aromatics Separation	Parex	C_8 aromatics	L	Sr-BaX
	Ebex	C8 aromatics	L	Sr-KX
Olefins from Paraffins	Olex	C4 distillate	L	--
Air Separation	O_2 production	Air	G	5A/13X
	N_2 production	Air	G	4A
Monosaccharide Separation	Sarex	Corn Syrup, Product of starch hydrolysis	L	CaY

*gas or liquid

TABLE 9

WORLD FCC CATALYST CONSUMPTION (tpa) (Ref 5)

Europe	36,000*
USA	170,000**
Rest of world	63,000*

* Assuming catalysts usage of 0.15 lbs per barrel oil

** Assuming catalyst usage of 0.20 lbs per barrel oil

TABLE 10

DETERGENT GRADE ZEOLITE MARKET AND PRODUCTION CAPACITY (Ref 38)

Country	Market (tpa) (approx.)	Capacity (tpa)
USA	70,000	140,000
Europe	190,000	205,000
Japan	100,000	110,000-150,000

Table 11

PROPERTIES OF FRESH AND EQUILBRIUM FCC CATALYSTS

	Amorphous * high alumina		Zeolite * XZ-2		** HEZ 55
	Fresh	Equilibrium	Fresh	Equilibrium	
Chemical analysis (dry basis), wt%					
Alumina	28	21.5	31	25.4	5.0
Carbon	0	0.20	0	0.25	
Sulfate	0.7	0.1	0.3	0.1	
Sodium	0.03	0.03	0.04	0.04	
Iron (ppm)	300	3900	700	3700	300
Metals (ppm of V+Ni+Cu)	0	162	0	259	<300
Physical properties					
Surface area, m^2/g	415	140	335	97	288
Pore volume, cm^3/g	0.88	0.43	0.60	0.45	0.4
Average bulk density, g/cm^3	0.39	0.70	0.52	0.68	0.9
Particle size, micromesh sieves, wt%					
0 to 20 um	2	0	2	0	
0 to 40 um	17	8	19	6	
0 to 80 um	68	69	75	75	
Average particle size, um	65	63	62	62	70
Catalytic activity					
Microavtivity, vol% conversion	60	59	85	73	

* Ref. 18

** Mobil 1988

Table 12

LINDE MOLECULAR SIEVE SPECIFICATION *

Type	3A	4A	5A	13X
Formula	$KaNA_{13}[(AlO_2)_{12}$ $(Si)_2)_{12}].27H_2O$	$Na_{12}[(AlO_2)_{12}$ $(SiO_2)_{12}].27H_2O$	$Ca_4Na_3[(AlO_212)$ $(SiO_2)_{12}].30H_2O$	$Na_{86}[(AlO_2)_{86}$ $(SiO_2)_{106}].XH_2O$
Pore Size A	3	4	5	10

General Physical Properties of the above microsieves

Heat of absorption	1.16 khw/kg
External surface area	1-3m^2/g
Internal surface area	700-800 m^2/g
Macro void volume	0.28-0.35 cm3/g
Specific Heat	0.25 cal/g/^{o}C

* Union Carbide Appendix I

Table 13

DESCRIPTION OF TYPE A ZEOLITE FOR LAUNDRY PRODUCT APPLICATION *

Description	A dried powered, crystalline product of aluminate, silicate, and caustic reaction in aqueous solution.
Appearance	Fine, white powder with no visible foreign impurties
Moisture	18-22%
Aluminum, Anhydrous Basis	18.0% minimum
Elemental Ratios Na:Al:Si	0.9-1.1/0.9-1.1/0.9-1.1
Crystalline Type A Zeolite	85% minimum vs. Standard Sample
Crystalline Hydroxysodalite	5% maximum vs. Standard Sample
Crystalline Quartz	1% maximum
Sizing	
- Individual Crystal Size (um)	6 expected maximum, never above 10
- Mean Particle Size (um)	4 expected maximum, never above 7.5
- Particle Size less than 1 um	10% maximum
Calcium Exchange Capacity, anhydrous basis	255 mg. ($CaCO_3$)/gram minimum
Causticity, (as Na_2O)	1.5% maximum
pH (1% slurry)	10.1-11.1
Dissolved metal Ion	<200 ppm

* Ref. 38 + Ethyl Spec. Appendix I

Table 14

SPECIFICATION PROPERTIES OF REFERENCE FILLERS *

Property	Reference Fillers $CaCO_3$**	Talc	Glass Spheres
Avg. Specfic Gravity (a)	2.71	2.85	2.48
Bulk Density, g/cm^3	1.15	--	--
Packing Factor, %	42.4	--	--
Particle Size, um:(b)			
Mean	3.5	7.6	31.7
Median	3.6	8.8	33.6
Surface Area, m^2/g(c)	3.26	17.50	0.10
Hegman Fineness (d)	6	4	3
Oil of Adsorption (e)	21.5	29	17.5
pH (f)	9.2-9.7	9.5	9.5
Dry Brightness, % (g)	94	89	61

(a) air pycnometer, ASTM D2840; (b) Coulter counter; (c) B.E.T. (nitrogen); (d) ASTM D1210; (e) ASTM D281; (f) ASTM D3100; (g) ASTM E97

* G.R. Gillet and J. Kriens "Ontario and the Mineral Fillers Industry", Industrial Minerals Background Paper No. 5 Ontario Ministry of Natural Resources

** Grade I Calcium Carbonate

Table 15

MECHANICAL PROPERTIES OF FILLED POLYPROPYLENE COMPOSITES SPECIFICATIONS

Filler	Filler Loading (% w/w)	Izod Impact (ft-lb/in)	Flexural Modulus (psi x 10^3)	Yield Strength (psi x 10^3)	Elongation at break (%)
Unfilled Polypropylene	--	1.3	135	3.4	93
Talc	20	0.8	247	3.3	15
	30	0.6	325	3.2	11
	40	0.5	379	3.2	8
$CaCO_3$ Grade I	20	0.9	192	2.9	33
	30	0.8	228	2.7	23
	40	0.7	281	2.7	12
Glass Spheres	20	0.8	167	2.7	19
	30	0.6	182	2.4	48
	40	0.6	217	2.1	43

Table 16

PHYSICAL CHARACTERISATION LEACH TAILS

	Sample I.D.	
	Caustic/Soda Ash Tails	Caustic Tails
DENSITIES (g/cc)	2.48	2.60
Wet	0.67	0.57
Tapped	0.79	0.59
Image Analysis		
Average Size (um)	13	14
OPTICAL ANALYSIS		
Average Size (um)	15	15
Geometric Mean (Standard Deviation)	1.9	1.9
COULTER ANALYSIS		
Sample (1) mean (um)	10.6	9.5
Sample (2) mean (um)	12.0	0.6
* SURFACE AREA (m^2/g)	38.2	59.3
* PORE VOLUME (cc/g) *	0.08	0.18
* AVERAGE PORE DIAMETER (A)	83.16	120.6
** OIL ADSORPTION	48.4	57.7
***pH	10.1	10.3

* From N_2BET measurements
** ASTM D281
*** ASTM D3100

Table 17

CHEMICAL ASSAY BULK SAMPLES

	3:1 Float Tails	Caustic Leach Tails	Caustic/Soda Ash Tails
SiO_2	49.69%	44.26%	42.48%
Al_2O_3	24.57	22.38	22.60
Fe_2O_3	10.03	9.10	9.19
CaO	2.19	2.36	2.03
MgO	1.31	1.38	1.24
Na_2O	0.74	7.60	8.88
K_2O	1.67	0.95	0.28
TiO_2	3.40	3.08	3.10
MnO	0.20	0.19	0.18
P_2O_5	0.27	0.23	0.22
V	2.6	.33	0.28
Ba	983 ppm	700 ppm	714 ppm
Sr	472	425	429
Zr	822	741	770
Be	5	5	5
Co	230	210	210
Cr	330	250	240
Cu	100	100	95
Pb	72	260	270
Ni	8400	8200	8600
Cd	<1	<1	<1
Ag	<1	<1	<1
Mo	650	35	4
Zn	210	190	250
Ammonium ppm	86	10.5	13.6
Nitrate (as N) ppm	<0.1	<0.1	2.8
Chlorine ppm	21	42	35
Sulphur %	0.11	0.060	0.13
Carbon %	0.60	1.00	1.30

Table 17 cont'd

	3:1 Float Tails	Caustic Leach Tails	Caustic/Soda Ash Tails
Scandium (Sc) ppm	19.0	4.0	36
Lanthanum (La) ppm	120.0	120	99
Cerium (Ce) ppm	200.0	210	170
Neodymium (Nd) ppm	110.0	96	76
Samardium (Sm) ppm	19.0	18	15
Europium (Eu) ppm	3.40	3.40	2.6
Terbium (Tb) ppm	1.5	2.40	1.5
Ytterbium(Yb) ppm	5.88	6.70	5.4
Lutecium (Lu) ppm	0.85	0.90	0.8
Uranium (U) ppm	11.0	10.0	9.1
Thorium (Th) ppm	38.0	34.	26.0
Gallium (Ga) ppm	--	10	10
Germanium (Ge) ppm	--	43	28
Yttrium (Y) ppm	--	110	110

Table 18

X-ray diffractions

RESEARCH

[illegible]

March 18, 1988

Craig Booth

REPORT NUMBER: X87306

IDENTIFICATION: Work Order No. 27826

SPECIFICATIONS Treated Tails

INTRODUCTION

Five mineral samples were presented for analysis by x-ray diffraction.

EXPERIMENTAL

Diffractometer traces were obtained using a Philips X-Ray Diffractometer with a copper target tube powered by a Philips constant potential X-Ray Generator.

RESULTS

The samples were, as labelled, of two distinctly different groups and will be reported as such.

FLOAT TAILS

The bulk of these samples was found to be amorphous with varying amounts of mullite ($Al_2O_3 \cdot SiO_2$), quartz (SiO_2) and in one case calcite ($CaCO_3$). All three samples contained approximately the same amount of unidentifiable material. The following tabulation lists the approximate concentrations in weight percent.

Sample	Amorphous	Quartz	Mullite	Calcite	Unident
J 3239 BHA FLOAT TAIL	Major	15	5-10	1-2	5-10
J 3240 ESP FLOAT TAIL	Major	6	2-5	-	5-10
J 3241 3:1 ESP: BHA TAIL	Major	4	2-5	-	5-10

Leach Tails

The major constituents in both samples was analcime ($NaAlSi_2O_6\ H_2O$).

Sample J 3242 contained sodium harmotome ($NaAl_2Si_6O_{16}\ 6H_2O$), while sample J 3243 contained a minor amount of calcite.

Both samples contained approximately equal amounts of quartz, and unidentifiable material, while the minor mullite content was slightly higher in J 3242 than in J 3243. The following tabulation lists the approximate concentrations in weight percent.

Sample	Analcime	Harmotome	Calcite	Mullite	Quartz	Unident
J 3242 NaOH Leach Tail	>50	10-20	-	2-5	≤1	5-10
J 3243 Na_2CO_3 Leach Tail	>70	-	2-5	1-2	≤1	5-10

T. Kilp

T.Kilp, Ph.D.
Section Manager

JW Jaremkow

J.W. Jaremkow
Project Technologist

ESP LEACHED TAIL (CAUSTIC/SODA ASH)

	D	I (MAX)	2THETA	FW WIDTH	H	K	L	IF
1	6.27601	0.40	14.100	0.00	0	0	0	0
2	5.62216	58.27 ✓	15.749	0.20	0	0	0	2
3	4.86507	12.90 ✓	18.217	0.22	0	0	0	2
4	4.59896	0.81	19.284	0.00	0	0	0	0
5	4.27333	1.34	20.769	0.17	0	0	0	2
6	3.85747	0.76	23.037	0.00	0	0	0	0
✓ 7	3.67989	9.05	24.165	0.24	0	0	0	2
8	3.44064	100.00 ✓	25.874	0.21	0	0	0	2
9	3.36619	1.58	26.456	0.25	0	0	0	2
10	3.23031	1.22	27.591	0.00	0	0	0	0
11	3.20472	0.50	27.815	0.23	0	0	0	2
12	3.04268	8.20	29.329	0.26	0	0	0	2
13	2.93245	52.28 ✓	30.458	0.21	0	0	0	2
14	2.85857	1.01	31.265	0.23	0	0	0	2
15	2.84331	0.69	31.437	0.21	0	0	0	2
16	2.81058	5.70 ✓	31.813	0.28	0	0	0	2
17	2.80700	5.80	31.854	0.26	0	0	0	2
18	2.77191	0.17	32.268	0.25	0	0	0	2
19	2.69837	14.39 ✓	33.173	0.24	0	0	0	2
20	2.61579	1.38	34.252	0.00	0	0	0	0
21	2.51122	13.58 ✓	35.725	0.26	0	0	0	2
22	2.47205	1.32	36.311	0.30	0	0	0	2
23	2.43254	6.00 ✓	36.922	0.34	0	0	0	2
24	2.36030	1.04	38.095	0.24	0	0	0	2
25	2.34469	0.96	38.358	0.24	0	0	0	2
26	2.29699	1.13	39.187	0.25	0	0	0	2
27	2.28471	0.78	39.406	0.26	0	0	0	2
28	2.25808	1.08	39.890	0.26	0	0	0	2
29	2.23097	6.38 ✓	40.396	0.26	0	0	0	2
30	2.20358	0.66	40.921	0.27	0	0	0	2
31	2.17649	1.25	41.453	0.25	0	0	0	2
32	2.12706	1.65	42.463	0.24	0	0	0	2
33	2.09609	0.82	43.121	0.28	0	0	0	2
34	2.04837	1.45	44.178	0.29	0	0	0	2
35	2.03682	4.06	44.442	0.36	0	0	0	2
36	2.03044	3.68	44.589	0.34	0	0	0	2
37	1.98805	0.57	45.592	0.20	0	0	0	2
38	1.95725	0.71	46.352	0.25	0	0	0	2
39	1.90883	7.38 ✓	47.599	0.42	0	0	0	2
40	1.90774	11.20 ✓	47.628	0.21	0	0	0	2
41	1.87137	6.62 ✓	48.612	0.24	0	0	0	2
42	1.84830	0.14	49.259	0.00	0	0	0	0
43	1.82596	0.04	49.903	0.24	0	0	0	2
44	1.81418	0.13	50.249	0.21	0	0	0	2
45	1.77052	0.72	51.579	0.21	0	0	0	2
46	1.74633	17.07 ✓	52.347	0.23	0	0	0	
47	1.71863	3.82 ✓	53.256	0.32	0	0	0	2
48	1.69322	6.15 ✓	54.120	0.24	0	0	0	2
49	1.66761	1.95	55.021	0.26	0	0	0	2
50	1.66331	0.69	55.175	0.27	0	0	0	2
51	1.64533	0.56	55.830	0.25	0	0	0	2
52	1.62091	1.75	56.747	0.30	0	0	0	2
53	1.61923	1.91	56.811	0.26	0	0	0	2
54	1.59885	5.32 ✓	57.602	0.25	0	0	0	2
55	1.57611	0.01	58.513	0.25	0	0	0	2
56	1.55860	0.98	59.236	0.23	0	0	0	2
57	1.54943	0.69	59.622	0.27	0	0	0	2
58	1.54513	0.10	59.805	0.26	0	0	0	2
59	1.54125	0.04	59.970	0.27	0	0	0	2
60	1.53749	0.46	60.132	0.29	0	0	0	2
61	1.52805	0.62	60.542	0.25	0	0	0	2
62	1.51092	0.84	61.302	0.25	0	0	0	2
63	1.50126	2.10	61.740	0.23	0	0	0	2
> 64	1.48305	3.97	62.583	0.24	0	0	0	2
65	1.47870	1.15	62.784	0.27	0	0	0	2
66	1.46214	0.74	63.581	0.28	0	0	0	2
67	1.45442	0.63	63.959	0.32	0	0	0	2
68	1.44993	2.15	64.180	0.28	0	0	0	2
69	1.44828	1.65	64.262	0.37	0	0	0	2
70	1.43675	0.05	64.841	0.26	0	0	0	2
71	1.43348	0.01	65.007	0.32	0	0	0	2
> 72	1.41762	5.67	65.826	0.27	0	0	0	2
73	1.41648	3.36	65.885	0.31	0	0	0	2
74	1.40414	0.36	66.539	0.22	0	0	0	2
75	1.38881	1.30	67.371	0.21	0	0	0	2
76	1.37567	2.78	68.102	0.22	0	0	0	2
77	1.37165	1.43	68.329	0.27	0	0	0	2
> 78	1.36153	9.06	68.900	0.21	0	0	0	2

ANALCIME DIFFRACTION PATTERN

X-Ray Powder Data (40)

hkl	d(A)	I
200[a]	6.87	< 10
211	5.61	80
220	4.86	40
321	3.67	20
400	3.43	100
332	2.925	80
422	2.801	20
431	2.693	50
521	2.505	50
440	2.426	30
611, 532	2.226	40
620	2.168	< 10
541	2.115	< 10

hkl	d(A)	I
631	2.022	10
543	1.940	< 10
640	1.903	50
633	1.867	40
642	1.833	< 10
732, 651	1.743	60
800	1.716	30
741	1.689	40
820	1.664	10
822, 660	1.618	20
831, 743	1.596	30

hkl	d(A)	I
842	1.498	20
761	1.480	20
664	1.463	10
754	1.447	10
932, 763	1.415	40
941, 853	1.386	<10
860	1.372	10
1011	1.359	40
1031	1.308	10
871	1.285	20
1033	1.263	20
963	1.220	30

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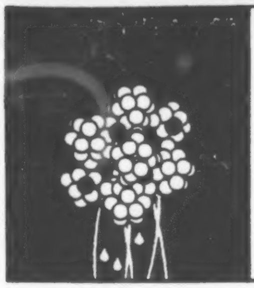
APPENDIX I SPECIFICATIONS



UNION CARBIDE Molecular Sieves adsorbent data

UNION CARBIDE Molecular Sieve Type 3A

DESCRIPTION

UNION CARBIDE Molecular Sieve Type 3A, the potassium form of the Type A Crystal structure, is an alkali metal alumino-silicate. Type 3A will adsorb molecules with critical diameters up to 3 angstroms.

APPLICATIONS

Type 3A is the preferred Molecular Sieve adsorbent for the commercial dehydration of unsaturated hydrocarbon streams such as cracked gas, propylene, butadiene, and acetylene. It is also used for drying polar liquids such as ethanol.

The small pore size of Type 3A prevents co-adsorption of hydrocarbons by excluding all other molecules while adsorbing water.

CHEMICAL FORMULA

$K_{12}\ [(AlO_2)_{12}(SiO_2)_{12}] \cdot X\ H_2O$

REGENERATION

UNION CARBIDE Molecular Sieve Type 3A can be regenerated for re-use by heating with simultaneous purge, or by evacuation. The degree of regeneration (water removal) is dependent on temperature and humidity of the purge gas.

SHIPPING INFORMATION

UNION CARBIDE Molecular Sieve Type 3A is available as powder, 1/16 in. and 1/8 in. pellets. It is shipped in non-returnable steel containers.

Container Size	Net Weight in lbs	
	Pellets	Powder
1 gal.	5	2
10 gals.	50	30
55 gals.	300	150

TYPICAL PROPERTIES	1/16" Pellets	1/8" Pellets	Powder
Nominal Pore Diameter	3 angstroms	3 angstroms	3 angstroms
Bulk Density	40 lb/cu ft	40 lb/cu ft	–
Hydrated Wet Density	–	–	2.03g/cc
Activated Dry Density	–	–	1.57g/cc
Particle Diameter	0.0575 in. to 0.0775 in.	0.115 in. to 0.135 in.	<10 microns*
Crush Strength	5.0 lbs	12.0 lbs	–
Crystal Structure	–	–	Cubic
Heat of Adsorption (max.)	1800 btu/lb H_2O	1800 btu/lb H_2O	1800 btu/lb H_2O
Equilibrium H_2O Capacity**	20% wt	20% wt	23% wt
Water Content (as shipped)	<1.5% wt	<1.5% wt	<2.5% wt
Molecules Adsorbed	Molecules with an effective diameter <3 angstroms, including H_2O, NH_3 and methanol		
Molecules Excluded	Molecules with an effective diameter >3 angstroms, e.g., ethane		

* Agglomerate particle size. Average crystal size is 1.0 to 4.0 microns

** Lbs H_2O / 100 lbs activated adsorbent at 17.5 mm Hg, 25°C.

UNION CARBIDE ADSORBENTS & CATALYSTS

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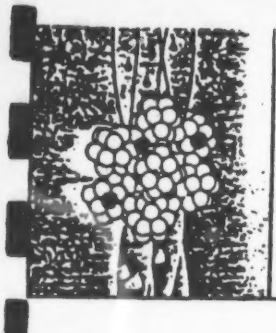

UNION CARBIDE
Molecular Sieves
adsorbent data

UNION CARBIDE
Molecular Sieve Type 4A

DESCRIPTION

UNION CARBIDE Molecular Sieve Type 4A, the sodium form of the Type A crystal structure, is an alkali metal alumino-silicate. Type 4A will adsorb molecules with critical diameters up to 4 angstroms.

APPLICATIONS

Type 4A is the preferred Molecular Sieve adsorbent for static dehydration in a closed gas or liquid system. It is used as a static desiccant in household refrigeration systems, in packaging of drugs, electronic components, and perishable chemicals, and as a water scavenger in paint and plastic systems. Type 4A is also used commercially in drying saturated hydrocarbon streams.

All molecules which can be adsorbed on Molecular Sieve Type 3A can be adsorbed on Molecular Sieve Type 4A.

CHEMICAL FORMULA

$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot X\,H_2O$

REGENERATION

UNION CARBIDE Molecular Sieve Type 4A can be regenerated for re-use by purging or evacuating at elevated temperatures. The degree of regeneration (water removal) is dependent on the temperature and humidity of the purge gas.

SHIPPING INFORMATION

UNION CARBIDE Molecular Sieve Type 4A is available in powder form, 1/16-in. and 1/8-in. pellets, 8 x 12 and 4 x 8 beads, and 14 x 30 mesh. It is shipped in non-returnable steel containers.

Container Size	Net Weight in lbs			
	Powder	Pellets	Beads	Mesh
1 gal.	2	5	5	5
10 gals.	30	50	50	50
55 gals.	150	300	300	300

TYPICAL PROPERTIES	1/16" Pellets	1/8" Pellets	14x30 Mesh	8x12 Beads	4x8 Beads	Powder
Nominal Pore Diameter	4 angstroms	4 angstroms	4 angstroms	4 angstroms	4 angstroms	4 angstroms
Bulk Density	41 lb/cu ft	41 lb/cu ft	40 lb/cu ft	42 lb/cu ft	40 lb/cu ft	–
Hydrated Wet Density	–	–	–	–	–	2.03 g/cc
Activated Dry Density	–	–	–	–	–	1.57 g/cc
Particle Diameter	0.0575 in. to 0.0775 in.	0.115 in. to 0.135 in.	0.0232 in. to 0.0555 in.	0.0661 in. to 0.0937 in.	0.0937 in. to 1.187 in.	<10 microns*
Crush Strength	9 lbs	17 lbs	–	6.9 lbs	18 lbs	–
Crystal Structure	–	–	–	–	–	Cubic
Heat of Adsorption (max.)	1800 btu/lb H_2O	1800 btu/lb H_2O	1800 btu/lb H_2O	1800 btu/lb H_2O	1800 btu/lb H_2O	1800 btu/lb H_2O
Equilibrium H_2O Capacity**	22% wt	22% wt	22% wt	22% wt	22% wt	28.5% wt
Water Content (as shipped)	<1.5% wt	<1.5% wt	<1.5% wt	<1.5% wt	<1.5% wt	<2.5% wt
Molecules Adsorbed	Molecules with an effective diameter <4 angstroms, including ethanol, H_2S, CO_2, SO_2, C_2H_4, C_2H_6, and C_3H_6					
Molecules Excluded	Molecules with an effective diameter >4 angstroms, e.g., propane					

*Agglomerate particle size. Average crystal size is 1.0 to 4.0 microns.

**Lbs H_2O / 100 lbs activated adsorbent at 17.5 mm Hg, 25°C.

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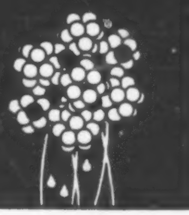

UNION CARBIDE
Molecular Sieves
adsorbent data

UNION CARBIDE Molecular Sieve Type 5A

DESCRIPTION

UNION CARBIDE Molecular Sieve Type 5A, the calcium form of the Type A crystal structure, is an alkali metal alumino-silicate. Type 5A will adsorb molecules with critical diameters up to 5 angstroms.

APPLICATIONS

Type 5A is the Molecular Sieve adsorbent which made possible the separation of normal paraffins from branched-chain and cyclic hydrocarbons through a selective adsorption process. It is now used commercially in large-scale n-paraffin separation processes.

All molecules which can be adsorbed on Molecular Sieve Type 3A and 4A can be adsorbed on Type 5A.

CHEMICAL FORMULA

$Ca_{4.5}Na_3\,[(AlO_2)_{12}(SiO_2)_{12}]\cdot X\,H_2O$

REGENERATION

UNION CARBIDE Molecular Sieve Type 5A can be regenerated for re-use by purging or evacuating at elevated temperatures. The degree of regeneration (water removal) is dependent on the temperature and humidity of the purge gas.

SHIPPING INFORMATION

UNION CARBIDE Molecular Sieve Type 5A is available as powder, 1/16-in. and 1/8-in. pellets. It is shipped in non-returnable steel containers.

Container Size	Net Weight in lbs	
	Pellets	Powder
1 gal.	5	2
10 gals.	50	30
55 gals.	300	150

TYPICAL PROPERTIES	1/16" Pellets	1/8" Pellets	Powder
Nominal Pore Diameter	5 Angstroms	5 Angstroms	5 Angstroms
Poured Density (average)	40 lb/cu ft	40 lb/cu ft	–
Settled Bulk Density	45 lb/cu ft	45 lb/cu ft	–
Hydrated Particle Density	–	–	2.03 g/cc
Activated Particle Density	–	–	1.57 g/cc
Particle Diameter	0.0575 in. to 0.0775 in.	0.115 in. to 0.135 in.	<10 microns*
Crush Strength	5.0 lb	12.6 lb	–
Crystal Form	–	–	Cubic
Heat of Adsorption (max.)	1800 btu/lb H_2O	1800 btu/lb H_2O	1800 btu/lb H_2O
Equilibrium H_2O Capacity**	21.5% wt	21.5% wt	28% wt
Water Content (as shipped)	<1.5% wt	<1.5% wt	<2.5% wt
Molecules Adsorbed	Molecules with an effective diameter <5 angstroms, including C_3H_8, n-C_4H_{10} to $C_{22}H_{46}$, n-C_4H_9OH and larger family members, R-12 and R-22		
Molecules Excluded	Molecules with an effective diameter >5 angstroms, e.g., iso compounds and all 4 carbon rings		

*Agglomerate particle size. Average crystal size is 1.0 to 4.0 microns.

**Lb H_2O / 100 lb activated adsorbent at 17.5 mm Hg, 25°C.

UNION CARBIDE **ADSORBENTS & CATALYSTS**

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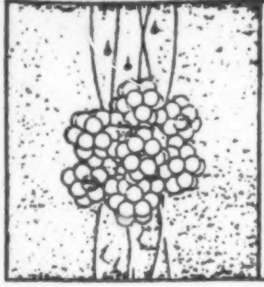

UNION CARBIDE
Molecular Sieves
adsorbent data

UNION CARBIDE Molecular Sieve Type 13X

DESCRIPTION

UNION CARBIDE Molecular Sieve Type 13X, the sodium form of the Type X crystal structure, is an alkali metal alumino-silicate. Type 13X will adsorb molecules with critical diameters up to 10 angstroms.

APPLICATIONS

Type 13X is used commercially for general gas drying, air plant feed purification (simultaneous removal of H_2O and CO_2) and liquid hydrocarbon and natural gas sweetening (H_2S and mercaptan removal).

All molecules which can be adsorbed on Molecular Sieve Types 3A, 4A, and 5A can be adsorbed on Type 13X. In addition, Type 13X can adsorb molecules of larger critical diameters, such as aromatics and branched-chain hydrocarbons.

CHEMICAL FORMULA

$Na_{86}\,[(AlO_2)_{86}\,(SiO_2)_{106}] \cdot X\,H_2O$

REGENERATION

UNION CARBIDE Molecular Sieve Type 13X can be regenerated for re-use by purging or evacuating at elevated temperatures. The degree of regeneration (water removal) is dependent on the temperature and humidity of the purge gas.

SHIPPING INFORMATION

UNION CARBIDE Molecular Sieve Type 13X is available as powder, 1/16-in. and 1/8-in. pellets. It is shipped in non-returnable steel containers.

Container Size	Net Weight in lbs	
	Pellets	Powder
1 gal.	5	2
10 gals.	50	30
55 gals.	275	150

TYPICAL PROPERTIES	1/16" Pellets	1/8" Pellets	Powder
Nominal Pore Diameter	10 angstroms	10 angstroms	10 angstroms
Bulk Density	38 lbs/cu ft	38 lbs/cu ft	–
Hydrated Wet Density	–	–	1.95 g/cc
Activated Dry Density	–	–	1.53 g/cc
Particle Diameter	0.0575 in. to 0.0775 in.	0.115 in. to 0.135 in.	<10 microns*
Crush Strength	10 lbs	18 lbs	–
Crystal Structure	–	–	Cubic
Heat of Adsorption (max.)	1800 btu/lb H_2O	1800 btu/lb H_2O	1800 btu/lb H_2O
Equilibrium H_2O Capacity**	28.5% wt	28.5% wt	34% wt
Water Content (as shipped)	<1.5% wt	<1.5% wt	<2.5% wt
Molecules Adsorbed	Molecules with an effective diameter <10 angstroms		
Molecules Excluded	Molecules with an effective diameter >10 angstroms, e.g., $(C_4F_9)_3N$		

*Agglomerate particle size. Average crystal size is 1.0 to 4.5 microns.
**Lbs H_2O / 100 lbs activated adsorbent at 17.5 mm Hg, 25°C.

UNION CARBIDE
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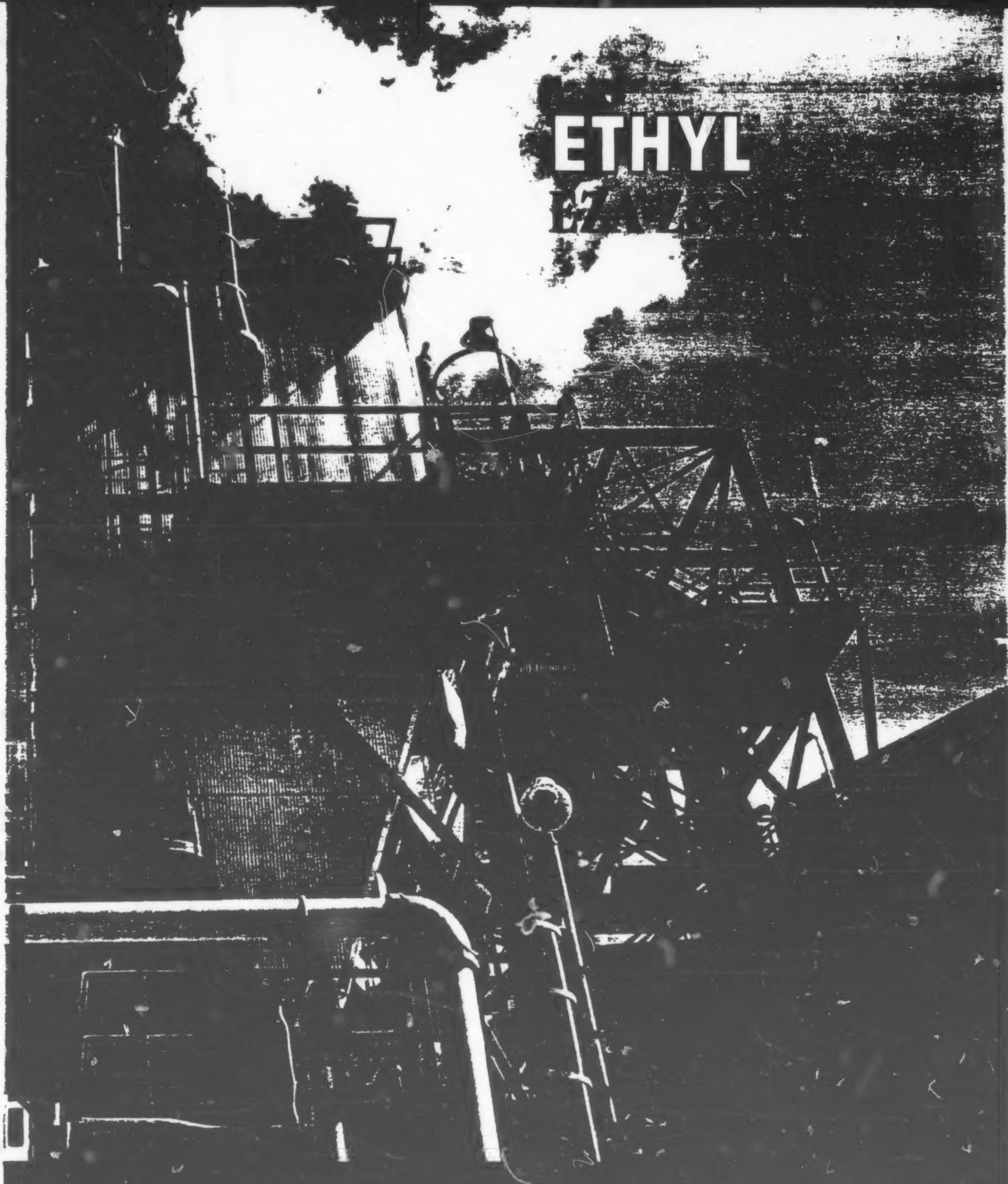
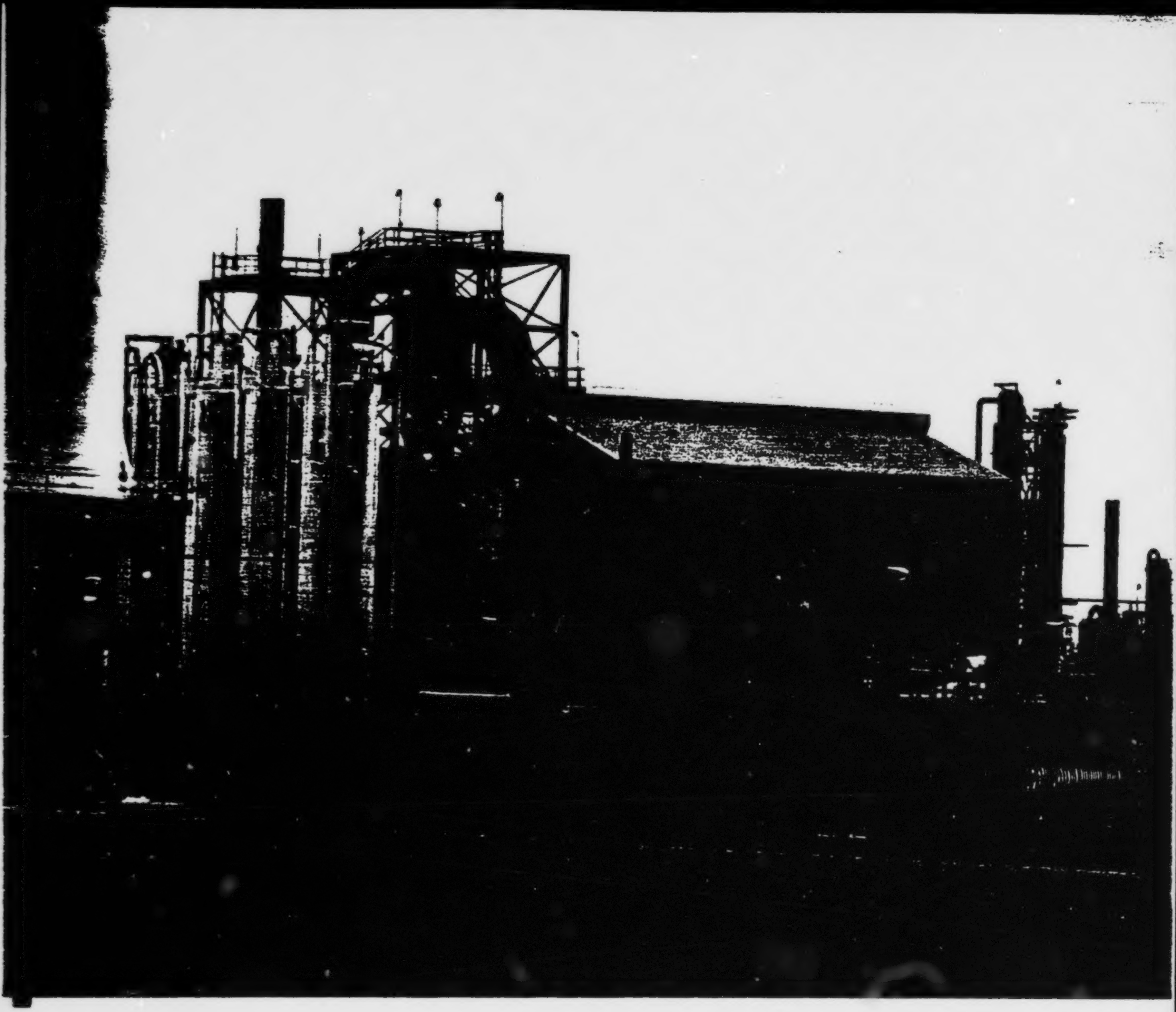


Ethyl has expanded its large commercial facility to help meet the world's growing need for synthetic Zeolite A.

Ethyl Chemicals Group



Ethyl™ EZA* Zeolite A is a crystalline molecular sieve with a high degree of structural ordering.

Physically, EZA* Zeolite A can be described as a hydrated sodium aluminosilicate, with the empirical formula: $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$

EZA* Zeolite A has an aluminate-silicate crystalline lattice, consisting of a network of interconnected cavities, 11.4 angstroms in diameter, which can be entered through uniform pore openings, 4.2 angstroms in diameter.

There is a very large internal surface area, occupied by the ion exchangeable sodium ions, and water, which can be reversibly removed through heat.

*Ethyl and EZA are trademarks of Ethyl Corporation

Its chemical and physical characteristics allow EZA* Zeolite A to selectively adsorb molecules and exchange ions.

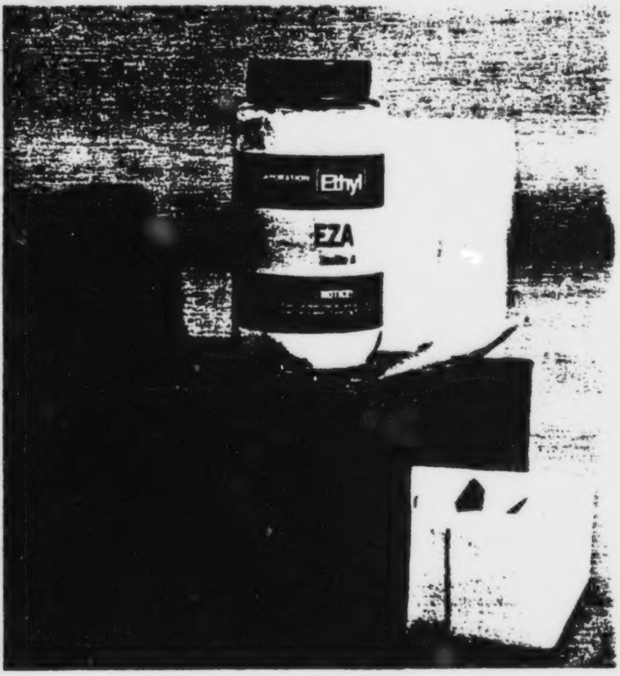
Pore size is one of the primary factors controlling entry into the internal structure. Critical diameters for some representative substances are shown in the table on the right (ion sizes are for the hydrated form).

CRITICAL DIAMETERS, A°

Substances	Angstroms
Ca^{++}	4.1
Na^{+}	3.6
NH_3	3.6
H_2S	3.6
H_2O	3.2
N_2	3.0
O_2	2.8
CO	2.8
CO_2	2.8
H_2	2.4

Ethyl: Large, Reliable, Proven.

Your source for Zeolite A.



Free samples are available for your evaluation.

Ask now for a sample to evaluate. To see how well EZA* Zeolite A meets your product requirements, simply call your Ethyl representative or one of our sales offices listed on the following page.

Potential applications seem limitless.

In detergents, where cost/performance is the name of the game, EZA* Zeolite A is an economically attractive and effective builder. It can also be used in dessicant systems or to separate gases. EZA* Zeolite A has great potential as a white pigment in paper, paint and plastics. It may find a home in carpet cleaners, dentifrices and flame retardants. Even animal nutritionists are studying the adsorbent properties of EZA* Zeolite A.

Ethyl's new expansion helps assure you continuity of supply.

Located in Houston, Texas, our manufacturing facility for synthetic zeolite A is one of the largest in the world. Our process is based on proven technology and secure raw material sources. On stream since 1978, we offer a product quality and uniformity that surpasses most natural sources.

Fast shipments made in bulk.

Our facilities are equipped to make fast deliveries in 5700 ft ^{3} pressure differential hopper cars. Highly qualified Ethyl technical representatives can provide on-site unloading assistance. Smaller developmental quantities can be arranged in 55 gallon nonreturnable steel drums and polypropylene bulk lift bags.

EZA* ZEOLITE A TYPICAL PROPERTIES

Description: EZA is Ethyl Corporation's brand of zeolite A. This product is a white, crystalline, sodium aluminosilicate hydrate powder

PROPERTY	TYPICAL VALUE
Crystallinity	85% Type A, minimum
Moisture	18.5 weight %
pH, 1% slurry	10-12
Calcium Exchange Capacity	>255 mg ($CaCO_3$)/gm
Mean Particle Size	3 microns

U.S. TSCA Chemical Inventory Registry Number CAS1344-00-9

For information about samples [illegible] Zeolite A, contact an Ethyl representative at the office [illegible]

ETHYL CORPORATION Ethyl Chemicals Group

DES PLAINES, IL
HOUSTON, TX
PARSIPPANY, NJ
SANTA ANA, CA
BRUSSELS
SINGAPORE
TORONTO

CALCIUM CARBONATE FILLERS

GRADE (ASTM-D-1199)	GRADE I	GRADE I	GRADE II	GRADE II	GRADE II	GRADE III	GRADE III	GRADE IV
PARTICLE SIZE ANALYSIS								
%Retained on 325 Mesh Sieve	0.005	0.01	0.02	0.02	0.0	1.0	1.0	22.0
Particle Size Range (Microns)	0.5-15.0	0.5-31.0	0.5-36.0	1.0-50.0	0.5	8.0	8.0	40.0
Mean Particle Size (Microns)	3.0	6.5	7.0	12.5	13.0	17.5	17.5	36.0
Hegman Grind	6-6¼	5-5¼	4-4¼	3				
PHYSICAL PROPERTIES								
Oil Absorption, ASTM-D-281 (lbs/100 lbs)	14.0-16.0	13.0-15.0	12.0-14.0	10.0-12.5				
Oil Absorption, ASTM-D-1483 (lbs/100 lbs)	15.0-17.0	13.5-15.0	13.0-15.0	11.0-13.0				
Loose Bulk Density (lbs/cu ft)	49.0	59.0	62.0	63.5	64.0	69.5	69.5	74.0
Bulking Value (gal/lbs)	0.0443	0.0443	0.0443	0.0443	0.0443	0.0443	0.0443	0.0443
Specific Gravity	2.71	2.71	2.71	2.71	2.71	2.71	2.71	2.71
Specific Resistance (ohms)	20,000	20,000	20,000	20,000	20,000	20,000	20,000	20,000
pH	9.4	9.4	9.4	9.4	9.4	9.4	9.4	9.4
Hardness (Mohs)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Refractive Index (mean)	1.59	1.59	1.59	1.59	1.59	1.59	1.59	1.59
Dry Brightness (minimum)	96.0	96.0	94.0	93.0	93.0	85.0	93.0	90.0
CHEMICAL COMPOSITION								
%Calcium Carbonate ($CaCO_3$)	98.00%	98.00%	98.00%	98.00%	95.00(min)	95.00(min)	95.00(min)	95.00(min)
%Magnesium Carbonate ($MgCo_3$)	0.60	0.60	0.60	0.60	3.00(max)	3.00(max)	3.00(max)	3.00(max)
%Silica (SiO_2)	0.50	0.50	0.50	0.50	1.00	1.00	1.00	1.00
%Iron Oxide (Fe_2O_3)	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
%Alumina (Al_2O_3)	0.36	0.36	0.36	0.36	0.36	0.36	0.36	0.36
%Moisture (H_2O)	0.02	0.02	0.02	0.02	0.02	0.15	0.15	0.15

APPENDIX II MICROSIEVE TESTING

NOVA HUSKY
RESEARCH
CORPORATION

NHRC Report No. 00335
Classification: Confidential

A COMPARATIVE EVALUATION
OF ZEOLITE E63
FOR MOISTURE ADSORBING CAPACITY

Prepared for:	Dr. Ian Todd Ontario Research Foundation
Author:	Charles Russell
Department:	Chemical Sciences Petrochemistry
Project:	Contract Project No. 688316

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4 Conclusions of the Study 9

1 OBJECTIVE OF THE STUDY

NOVA HUSKY RESEARCH CORPORATION (NHRC) was approached by Dr. Ian Todd of the Ontario Research Foundation to assist in evaluating the commercial worth of a zeolite (E63) which is the by-product of an undisclosed process. NHRC's involvement was restricted to evaluating the zeolite's molecular sieve capabilities.

It was decided, through verbal discussions with Dr. Todd, to limit initial evaluations to a small comparative study designed to assess the capacity of the zeolite to adsorb moisture. Pending the results of this study, additional assessment could be conducted in the future to better ascertain the molecular sieve characteristics of the zeolite.

2 SCOPE OF THE STUDY

Details of the zeolite, supplied by Dr. Ian Todd, indicated that the zeolite had a surface area of 40-60 m^2/g and a pore diameter of approximately 80 angstroms. Because of the large pore diameter it was decided that the comparative evaluation should be conducted using a commercially available zeolite also having a relatively large pore diameter.

The moisture adsorbing capacity of zeolite E63 was comparatively assesssed using a Union Carbide* 13X zeolite as the reference material. Since the E63 zeolite was supplied as a powder, the reference material used in the study was also in powder form (no binders were present). Some of the typical properties of the two zeolites are noted in Table I.

TABLE 1 COMPARISON OF ZEOLITE PROPERTIES

Property	Zeolite E63	Zeolite 13X
Surface Area	40-60 m^2/g	300 m^2/g
Pore Diameter	80 A	10 A
Bulk Density (tapped)	1.20 g/cc	0.51 g/cc
Initial H_20 Content	5.7wt%	2.5wt%
Equilibrium H_2O Capacity	?	26wt%

---

* The Union Carbide Corporation, USA

Initial assessment of the moisture capacity of zeolite E63 was performed using a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The GC was configured in such a way as to minimize the distance from the injector port to the zeolite column and the distance of the zeolite column to the detector. A small length of 1/16" 316SS tubing was used to connect the exit of the injector port to the bottom of a 1/8" X 3" 316SS column containing the zeolite (small, glass wool plugs were used at both ends of the 1/8" column to hold the zeolite). The column of zeolite was connected directly to the entrance of the TCD.

To assess the moisture capacity of the zeolite approximately 0.2 grams of the material was activated in the GC (350°C for approximately 17 hours) using the packed column arrangement and a small flow of dry helium. The activated zeolite was then cooled to 100 °C and saturated by the injection of small aliquots of water. The zeolite was then allowed to equilibrate at 100°C until the amount of moisture eluting from the sieve was considered to be insignificant (typically 1 to 3 hours). The moisture eluting from the sieve was followed by monitoring the TCD sensor output.

After equilibration at 100°C, the sieve was rapidly heated to 350°C and the amount of water desorbed from sieve was measured by integration of the signal from the TCD. The adsorption/desorption process was repeated with the zeolite sample to examine the influence of multiple activation cycles on the sieve performance.

A similar evaluation was conducted on the Union Carbide* 13X zeolite.

In addition to the chromatographic studies, the zeolites were also examined using the thermal gravimetric analysis (TGA) techniques. A total of six samples (see Table 2) were analyzed. The thermal analysis involved heating the sieve at a temperature of 45°C for 30 minutes, ramping the temperature to 200°C at a rate of 25°C/min, holding the temperature at 200°C for two hours and then ramping the temperature to 350°C (25°C/min) and holding at that temperature for another two hours. The weight loss at each of the temperature plateaus was then used to define the adsorption/desorption characteristics of the sieves.

---

[*] The Union Carbide Corporation, USA

TABLE 2 SUMMARY OF SAMPLES USED IN THERMAL ANALYSIS STUDY

Sample	Zeolite	Status	Treatment
1	E63	Unactivated	Equilibrated at Room Conditions
2	E63	Activated	Equilibrated at Room Conditions
3	E63	Activated	Equilibrated over H_2O
4	13X	Unactivated	Equilibrated at Room Conditions
5	13X	Activated	Equilibrated at Room Conditions
6	13X	Activated	Equilibrated over H_2O

3 RESULTS AND DISCUSSION

3.1 Chromatographic Study

Initially, the adsorption characteristics of the zeolites were to be studied by measuring the amount of moisture trapped on the zeolite upon successive injections of water at a temperature of 40°C. The amount of adsorbed moisture was to be estimated by subtracting the amount of moisture which eluted from the actual volume injected. Difficulties were encountered with this procedure in that temperature and adsorption/desorption equilibration factors caused extensive broadening and tailing of the moisture peak, thus making quantification of the mositure peak unreliable. Elevation of the GC temperature to 100°C improved the peak shape somewhat; however, the accuracy of the integration method was still inadequate.

In light of these results it was decided to estimate the adsorption capacity of the zeolites by saturating the zeolite at a temperature of 100°C, allowing the zeolite to equilibrate and then desorbing the remaining moisture by elevating the temperature to 350°C. Using this procedure, the peak shape of the desorbed moisture was improved and more reliable estimations could be obtained.

During the GC study it was determined that a calibration of the TCD moisture response was required for each zeolite and that the response was influenced by the temperature of the GC oven. The calibrations for the zeolites were established by saturating the particular zeolite and then injecting a known amount of additional water into the GC. Assuming that all of the moisture eluted from the zeolite, the corresponding peak area was used to determine the TCD response factor. This calibration method was performed for GC oven temperatures of 100°C and 350°C (temperature of adsorption and desportion) for each zeolite.

The results of the calibrations are noted in Figures 1 and 2 for the E63 and 13X zeolites, respectively. The response factors for the various temperatures and zeolites was not expected to vary as much as that observed. The reason for the differences in TCD response can be attributed, at least in part, to the changing shape of the eluting moisture peak. Differences in the packing of the zeolite and the affinity of the zeolite towards moisture served to alter the shape and retention time of the moisture peak and this may have influenced the sensitivity of the TCD.

The integrated results of the desorption experiment are summarized in Table 3. The E63 zeolite was saturated and desorbed a total of four times while the 13X zeolite was cycled through the saturation/desorption process three times. For each desorption experiment the amount of moisture not adsorbed and the amount obtained by the thermal desorption step was noted. This allowed one to monitor a "mass balance" for each experiment (see "% OF VOLUME INJECTED", Table 3). The values quoted in Table 3 for the amount of moisture not adsorbed by the zeolite ("AMOUNT ELUTED") were obtained using the corresponding 100°C calibration curve. The desorption values in Table 3 ("AMOUNT DESORBED") were obtained similarly, using the 350°C calibration curve. Since the desorption temperature ranged from 100°C to 350°C, the values quoted in Table 3 slightly underestimate the actual capacities. Only a small portion of the moisture was observed to be desorbed at the lower temperatures, thus the errors introduced by the use of the 350°C calibration was not considered to be very large.

The results obtained for E63 were fairly consistant for all four of the desorption cycles. The consistant results, together with the good accountability for the total amount of injected water, expresses a degree of reliability for the method. Based on the amount of zeolite used in the experiments (0.22g) and the initial moisture content of the zeolite (measured to be 5.7wt%), the average amount of desorbed moisture from the four cycles (3.9µl) corresponds to a dry weight capacity of 1.9wt%.

The three 13X desorption experiments also yielded fairly consistent desorption data. The average amount of desorbed moisture, 19.9µl, corresponds to a dry weight moisture capacity of 13.6 wt% (amount of 13X zeolite used was 0.15g with an initial moisture content of 2.5 wt%).

The "mass balance" for the 13X experiments was not as good as that obtained with the E63 experiments. The reason for this would appear to be due to the non-linear TCD response curve which was obtained for the 13X - 100°C (see Figure 2). The affinity of the zeolite for moisture resulted in extensive peak tailing at the 100°C temperature and this did not allow for accurate peak integrations.

To ascertain if indeed the 13X zeolite sample had a 20µl capacity for water the last experiment noted in Table 3 (Experiment 7) was conducted by first injecting 20µl of water at 100°C. The additional 10µl (for a total of 30µl) was injected subsequently. The TCD sensor output was monitored for two hours after the 20µl injection and no moisture was observed eluting from the zeolite. The injection of the additional 10µl of water resulted in a measured elution of 9µl, as noted in Table 3. The fact that no moisture was detected after the 20µl injection confirmed the relatively large moisture affinity of the zeolite.

TABLE 3 GC THERMAL DESORPTION DATA*

Experiment Number	Zeolite	Amount Injected	Amount Eluted	Amount Desorbed	% of Vol. Injected
1	E63	40	--	5.2	--
2	E63	40	34.1	3.4	94
3	E63	40	34.7	3.5	96
4	E63	40	35.7	3.5	97
5	13X	40	14	17.9	80
6	13X	30	8	20.1	94
7	13X	30	9	21.7	102

* amount in μl, desorption from 100°C to 350°C

3.2 Gravimetric Study

In view of the difficulties that were observed in obtaining quantitative desorption data with the GC method, a gravimetric thermal analysis (TGA) was also performed on the zeolites.

Six experiments were conducted as noted in Table 2. The activated zeolite samples used in the TGA study were heated in an oven at a temperature of 350°C for 17 hours. The samples that were exposed to "room conditions" were placed in a petri dish and left out in the open for a minimum of ten days prior to analysis. The samples equilibrated over water were supported in a desiccator containing 1" of water and were also allowed to equilibrate for a minimum of ten days.

The results of the TGA studies are shown in Figures 3 to 9 and the weight loss data from the experiments are summarized in Table 4, along with calculated moisture capacities. The data in Table 4 has been corrected for buoyancy effects, caused by changes in the density of the air in the sample chamber (see Figure 9). The moisture capacities in Table 4 have been calculated by converting the corrected 350°C weight loss data to a dry basis [x/(1-x)].

In general, the zeolite moisture capacities, as measured by TGA, tend to be in agreement with the chromatographic results. The slightly higher moisture contents observed using the TGA method are a result of measuring total moisture content of the zeolite starting from ambient temperature (as opposed to 100°C with the chromatographic method).

The moisture capacities measured by TGA for the 13X zeolite are in good agreement with the reported equilibrium value of 26wt%, while the moisture data obtained in Experiments #4 and #5 for zeolite E63 (5.4% and 2.7%, respectively) agree well with the values determined using the chromatographic method (ie., 5.7% for the raw zeolite and 1.9% for the activated zeolite).

Although the E63 zeolite showed some appreciable moisture uptake when equilibrated over water (15.5wt%, Table 4, Experiment 3), the moisture was very loosely adsorbed, as evidenced by the loss of 8.6wt% during the 45°C stabilization period. Figure 5 indicates that for this experiment the moisture was still desorbing from the zeolite at the end of the 45°C holding period.

TABLE 4 RESULTS OF TGA STUDY ON ZEOLITES E63 AND 13X*

Temp.	Time	Zeolite E63(Wt%)			Zeolite 13X(Wt%)		
(°C)	(Min.)	Exp.1	Exp.2	Exp.3	Exp.4	Exp.5	Exp.6
45	40	0.2	0.2	8.6	1.0	1.1	2.8
200	166	3.0	1.9	10.8	17.0	17.0	19.8
350	292	5.1	2.6	13.4	21.0	21.0	23.7
MOISTURE CAPACITY		5.4	2.7	15.5	26.6	26.7	31.1

* Data has been corrected for buoyancy: 45°C - by 0.3%, 200°C - by 0.94%, 350°C - by 1.30%
(i.e., if measured loss at 350°C was 1.3%, then corrected loss is 2.6%)

4 CONCLUSIONS OF THE STUDY

Both the chromatographic and gravimetric data indicate that the E63 zeolite has a significantly lower capacity for adsorbed moisture when compared to the commercial 13X zeolite from Union Carbide*. Based on the TGA results, the E63 zeolite adsorbed only 2.7wt% moisture following activation, whereas the 13X zeolite adsorbed 26.7wt% by comparison.

Although the zeolites were evaluated by studying only the desorption characteristics of the material the information obtained appears to be decisive. The E63 zeolite demonstrated an affinity for moisture in only one experiment (where the material was equilibrated over water in a sealed container). The TGA results for this experiment indicated that the water was very loosely bound to the zeolite surface.

The difficulties encountered with the chromatographic method during calibration of the TCD response factor and peak integration leads one to believe that the gravimetric data is more accurate and that the method is, therefore, more appropriate for evaluating moisture capacities of zeolites. The chromatographic method may, on the other hand, be more appropriate for zeolite evaluations which involve the adsorption/desorption of more volatile components.

It would appear from the results of this study that zeolite E63 does not have sufficient moisture capacity for it to be of any commercial significance. In view of the zeolite's low affinity for moisture and large pore size it is not likely that the zeolite would have any commercial value as a molecular sieve for adsorbing most non-polar and polar components.

* The Union Carbide Corporation, USA

FIGURE 1: TCD RESPONSE TO MOISTURE CALIBRATION FOR ZEOLITE E63

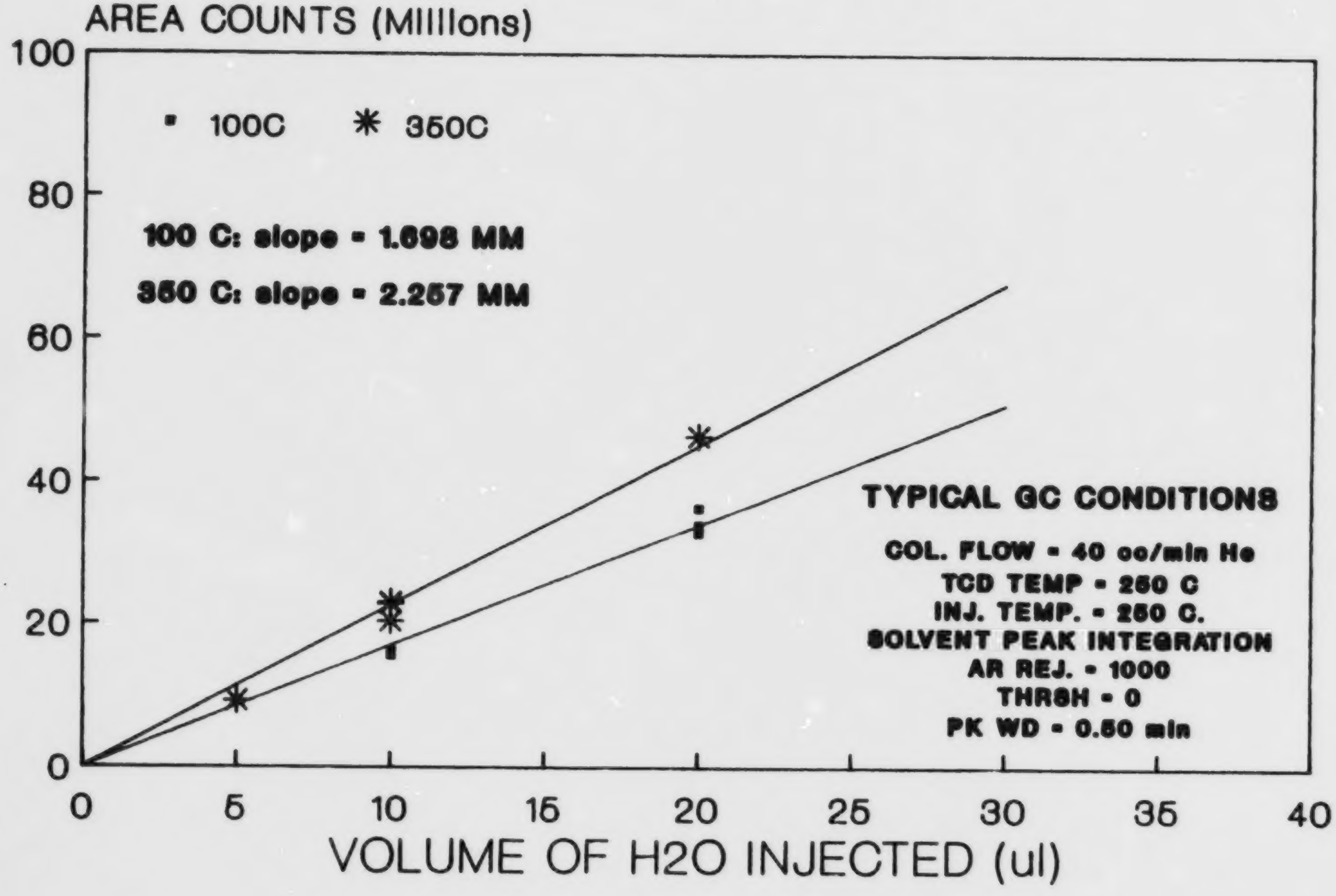
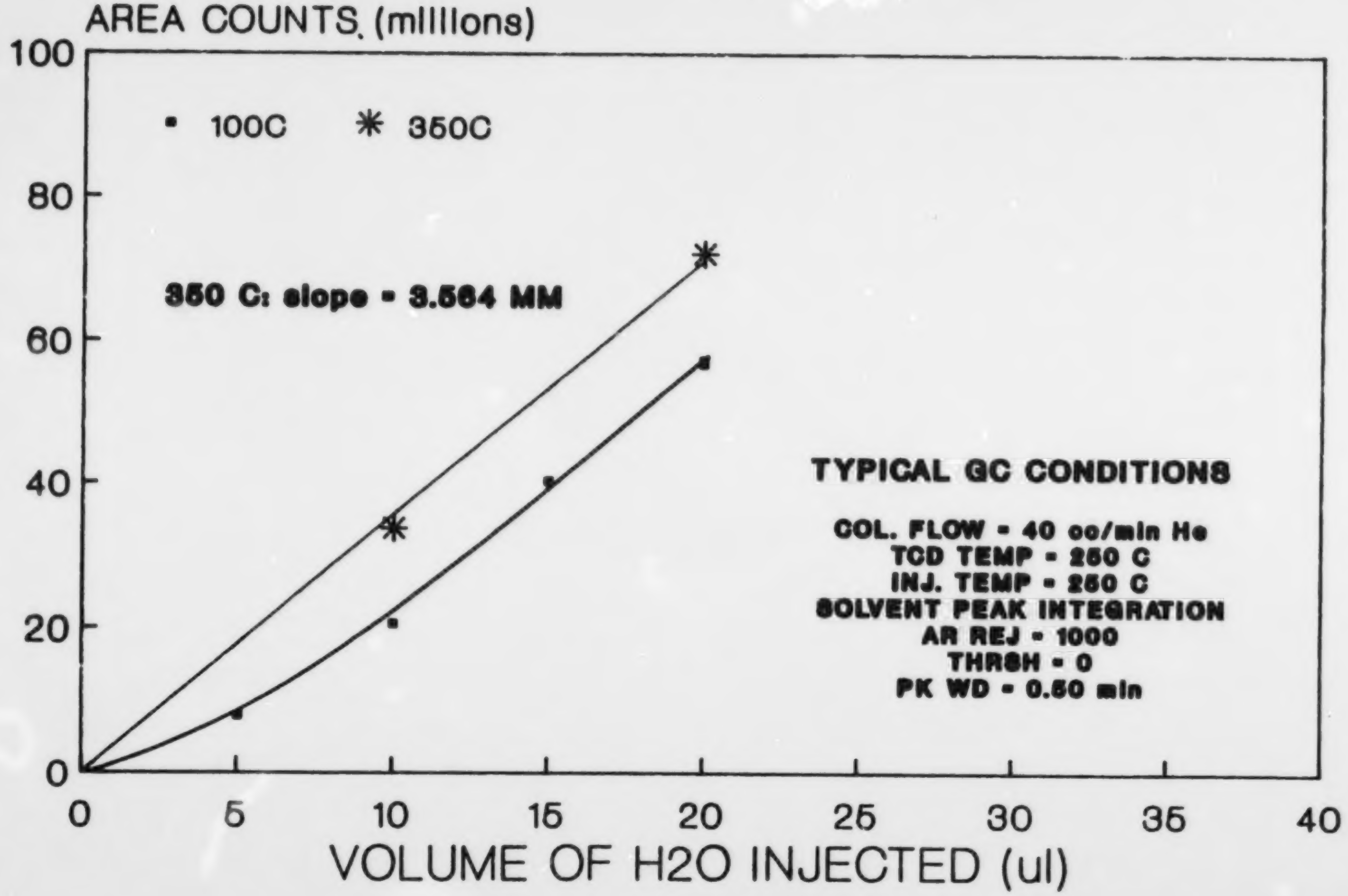


FIGURE 2: TCD RESPONSE TO MOISTURE CALIBRATION FOR ZEOLITE 13X



[redacted] F[redacted]RE [redacted] E[redacted]Zed[redacted]te, [redacted]act[redacted]ate[redacted] Eq[redacted]ib[redacted]ed [redacted] Ro[redacted]Con[redacted]tio[redacted] [redacted] [redacted] [redacted] [redacted]e 1[redacted]

OPERATOR:	R.SAETRE	NETZSCH STA 429/409		ATM.	AIR	
DATE:	03/25/88	REFERENCE :	AL203	FLOW =	0 cc/min	
RUN No.	4	CRUCIBLE :	AL203	HEAT RATE =	25 C/min	
TG Setting	50mg	FILE NAME :	ZE63EQUN	SAMPLE WT.=	48.9 mg	
DTA Setting	0.1mV	MATERIAL	ZEOE63	REF WEIGHT	0 mg	

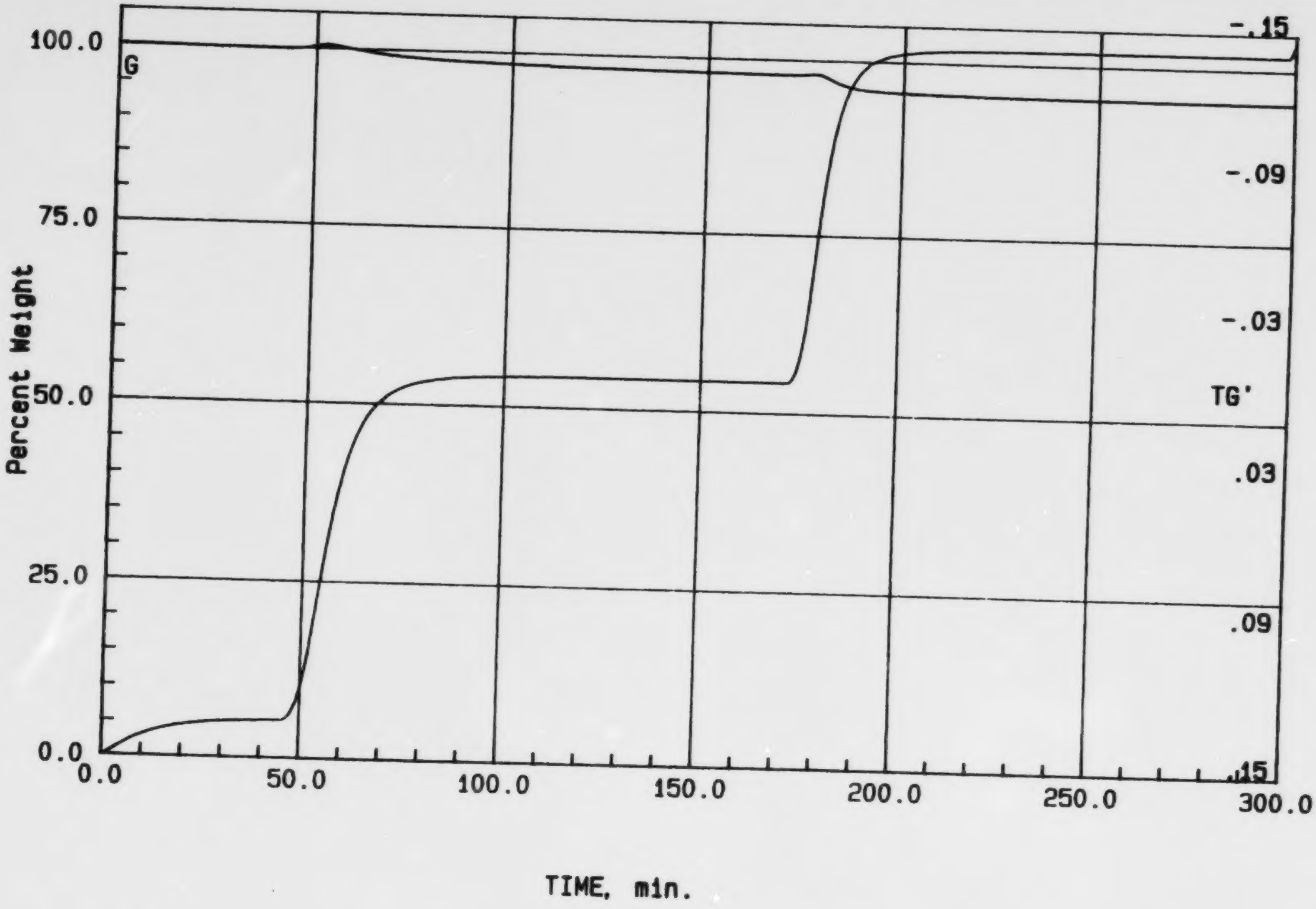


FIGURE 4: E63 Zeolite, Activated, Equilibrated at Room Conditions

OPERATOR: R.SAETRE
DATE: 03/29/88
RUN No. 7
TG Setting 50mg
DTA Setting 0.1mV

NETZSCH STA 429/409
REFERENCE : AL203
CRUCIBLE : AL203
FILE NAME : ZE63EQAC
MATERIAL ZEOE63

ATM. AIR
FLOW = 0 cc/min
HEAT RATE = 25 C/min
SAMPLE WT.= 48.9 mg
REF WEIGHT 0 mg

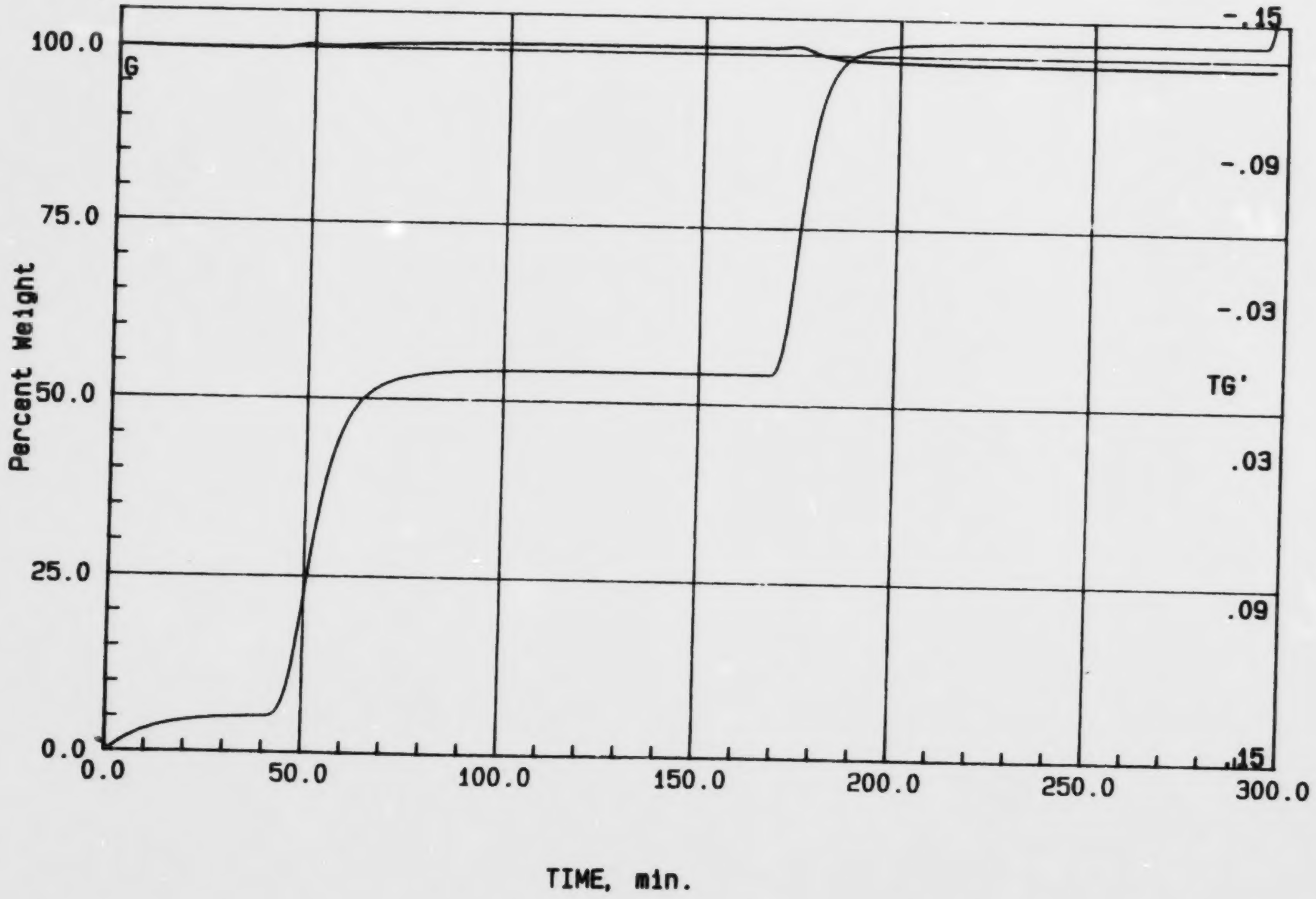


FIGURE 5: E63 Zeolite, Activated, Equilibrated over H_2O

OPERATOR:	R.SAETRE	NETZSCH STA 429/409		ATM.	
DATE:	03/24/88	REFERENCE :	AL203	FLOW =	0 cc/min
RUN No.	1	CRUCIBLE :	AL203	HEAT RATE =	25 C/min
TG Setting	50mg	FILE NAME :	ZE63HYD1	SAMPLE WT.=	43.2 mg
DTA Setting	0.1mV	MATERIAL	ZEOE63	REF WEIGHT	0 mg

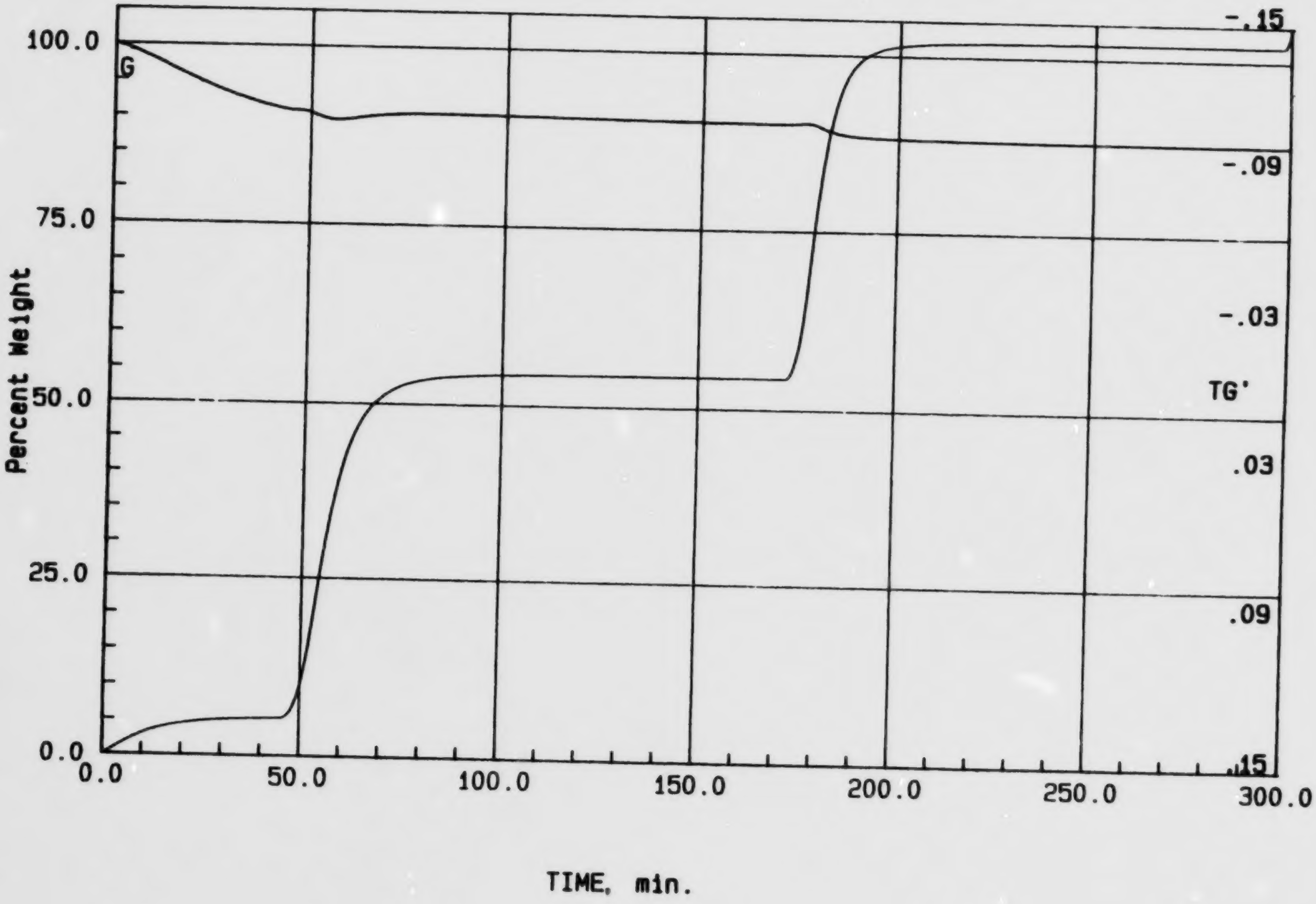


FIGURE 6: 13X Zeolite, Unactivated, Equilibrated at Room Conditions

OPERATOR:	R.SAETRE	NETZSCH STA 429/409		ATM.	AIR	
DATE:	03/28/88	REFERENCE :	AL203	FLOW =	0 cc/min	
RUN No.	5	CRUCIBLE :	AL203	HEAT RATE =	25 C/min	
TG Setting	50mg	FILE NAME :	ZE13EQUN	SAMPLE WT.=	47.3 mg	
DTA Setting	0.1mV	MATERIAL	ZE013X	REF WEIGHT	0 mg	

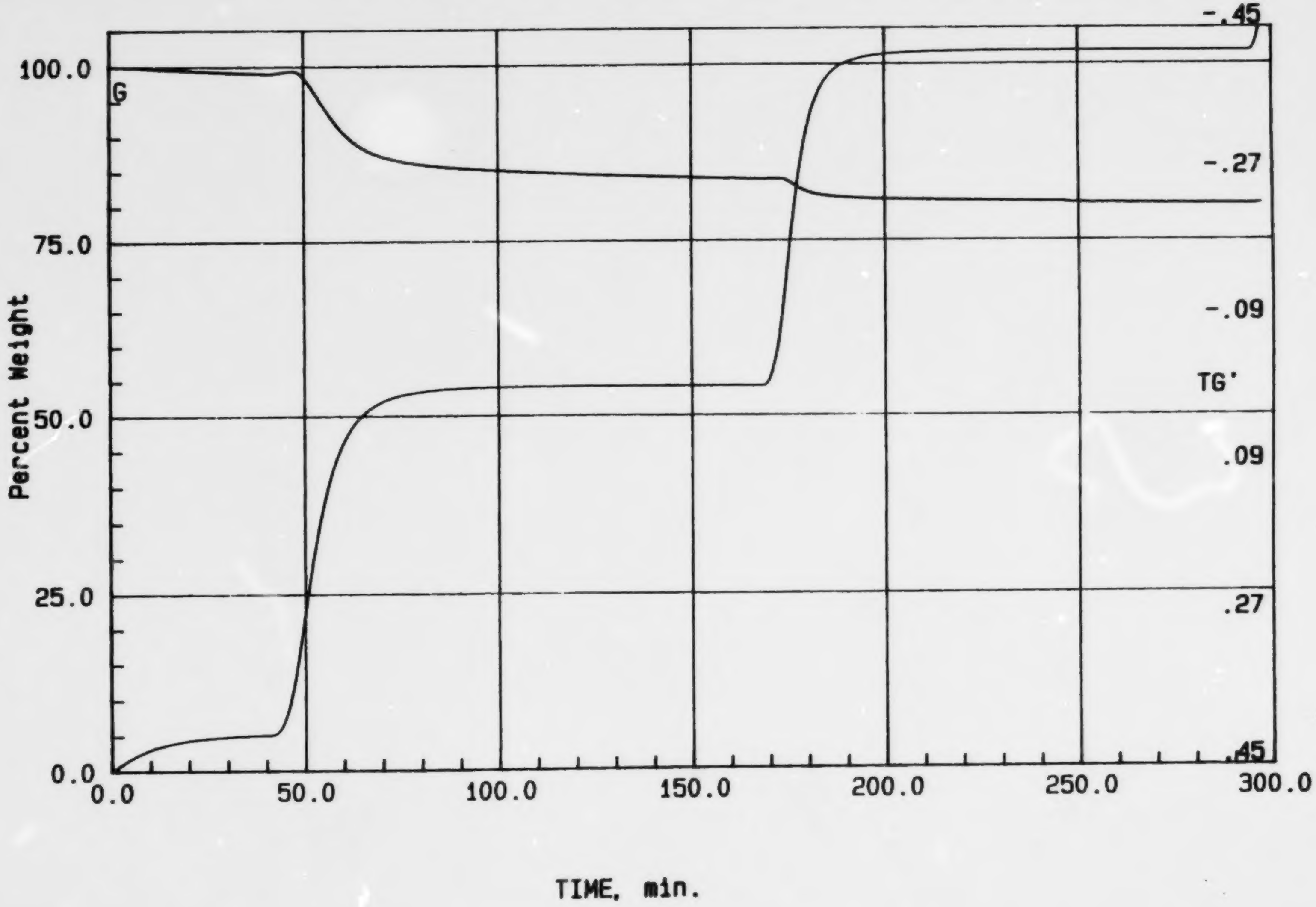


FIGURE 7: 13X Zeolite, Activated, Equilibrated at Room Conditions

OPERATOR: R.SAETRE		NETZSCH STA 429/409		ATM.	AIR	
DATE:	03/29/88	REFERENCE :	AL203	FLOW =	0 cc/min	
RUN No.	8	CRUCIBLE :	AL203	HEAT RATE =	25 C/min	
TG Setting	50mg	FILE NAME :	ZE13EQA2	SAMPLE WT.=	48 mg	
DTA Setting	0.1mV	MATERIAL	ZE013X	REF WEIGHT	0 mg	

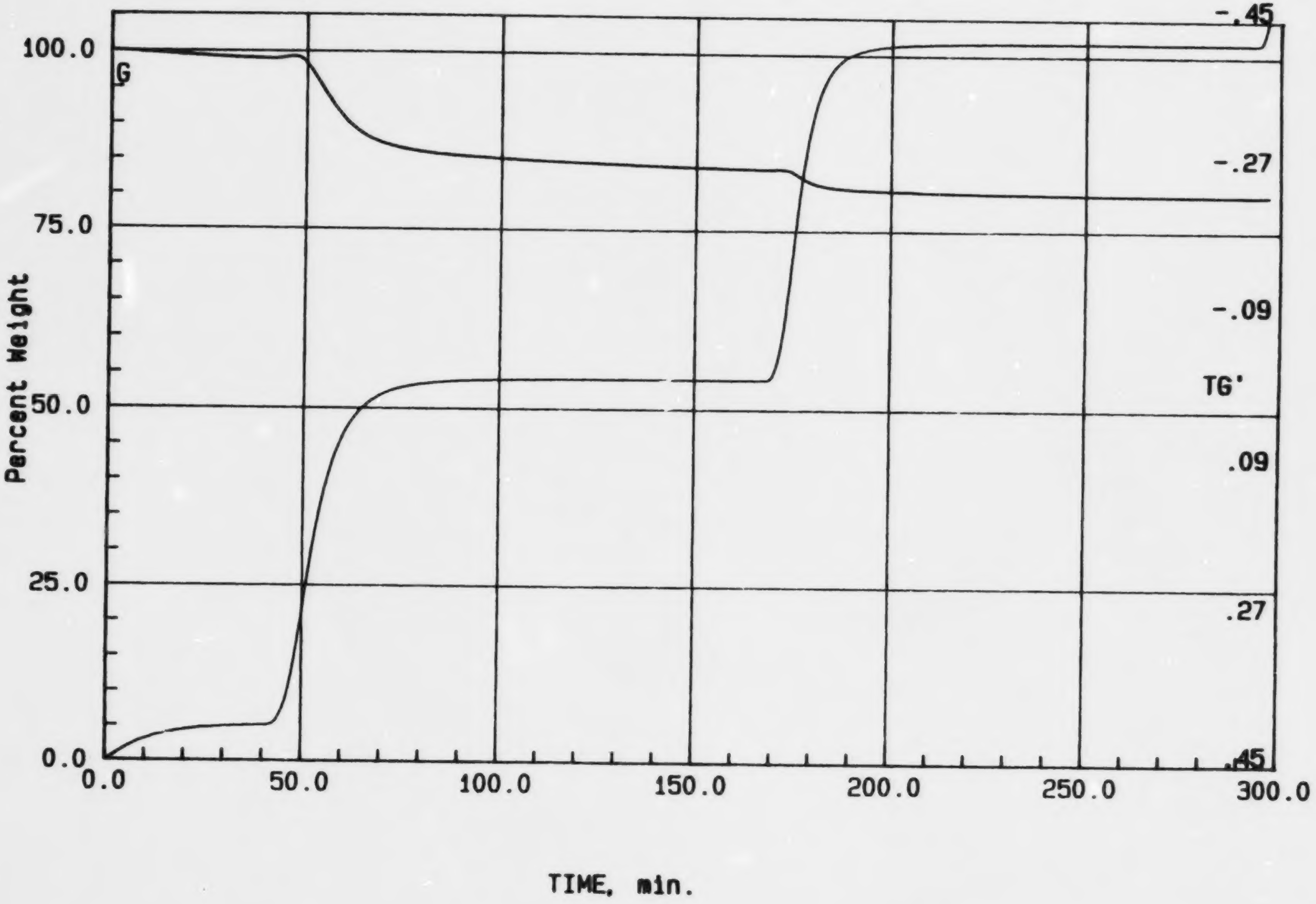


FIGURE 8: 13X Zeolite, Activated, Equilibrated over H_2O

OPERATOR: R.SAETRE		NETZSCH STA 429/409		ATM.	AIR	
DATE:	03/25/88	REFERENCE :	AL203	FLOW =	0 cc/min	
RUN No.	3	CRUCIBLE :	AL203	HEAT RATE =	25 C/min	
TG Setting	50mg	FILE NAME :	Z13XHYD2	SAMPLE WT.=	43.2 mg	
DTA Setting	0.1mV	MATERIAL	ZE013X	REF WEIGHT	0 mg	

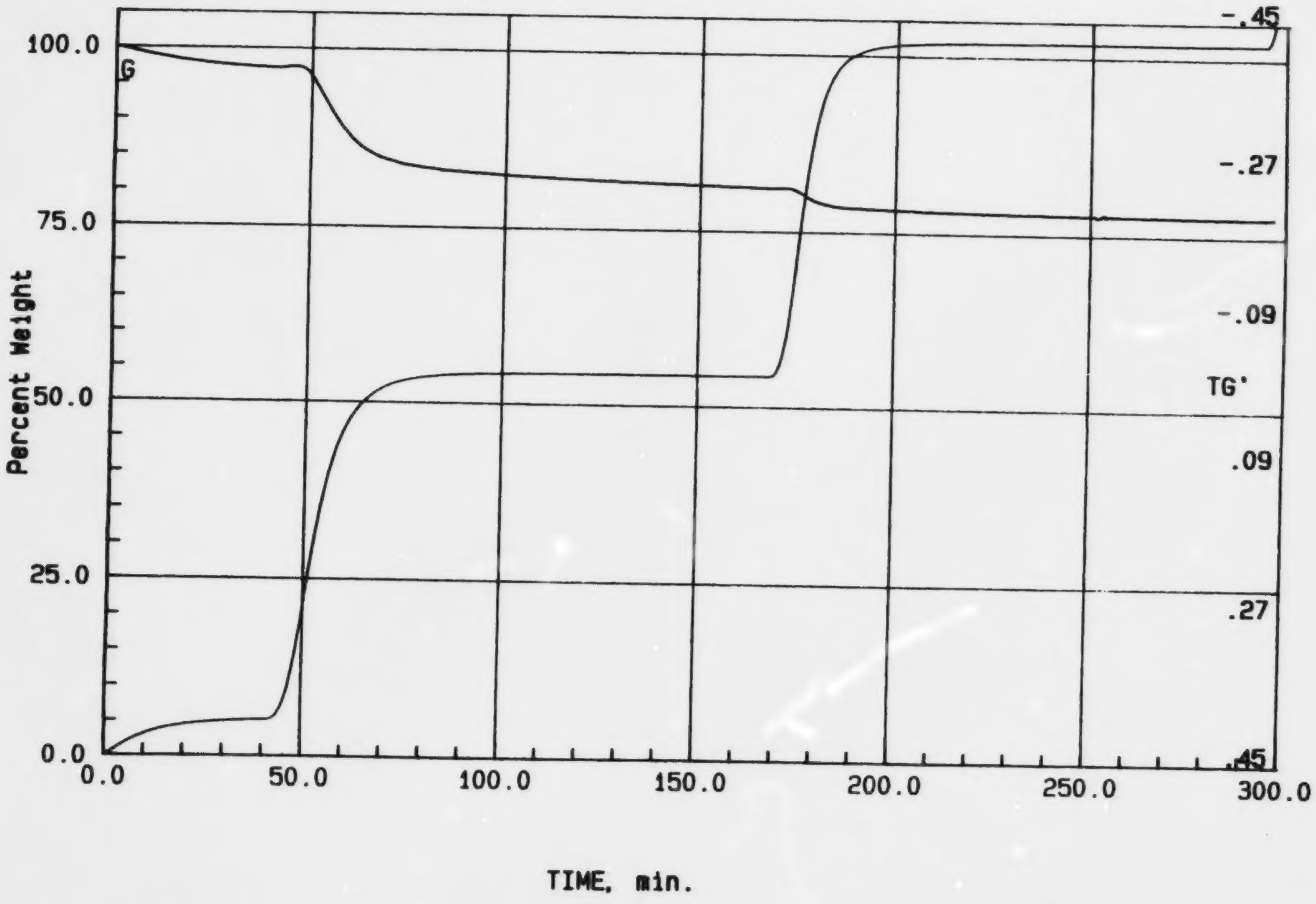
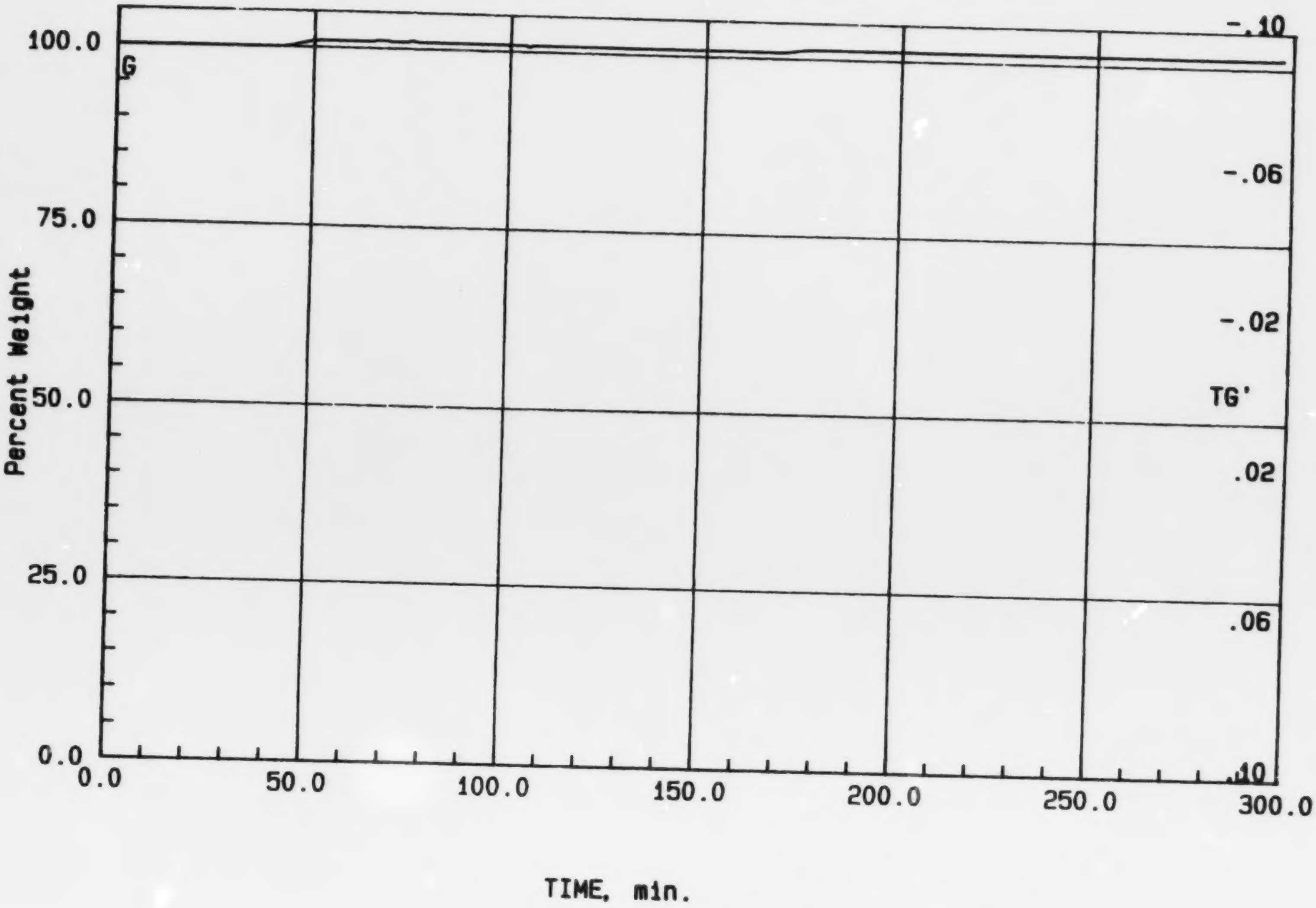


FIGURE 9: Blank Run to Determine Buoyancy Effect

OPERATOR: R.SAETRE	NETZSCH STA 429/409	ATM. AIR	
DATE: 03/30/88	REFERENCE : AL203	FLOW = 0 cc/min	
RUN No. 9	CRUCIBLE : AL203	HEAT RATE = 25 C/min	
TG Setting 50mg	FILE NAME : ZEOBLANK	SAMPLE WT.= 48 mg	
DTA Setting 0.1mV	MATERIAL ZEOBLANK	REF WEIGHT 0 mg	



APPENDIX III PLASTIC FILLER TESTING

May 12,1988

Mr. Iain Todd
MRCCR

Report Number	PT 3211-88-1
Identification	Re: W.O. #30256
Specification Of Order	Powder Filler Testing

INTRODUCTION

A powder filler, designated Carbovan #41-10874 NaOH (150 Kg/T) Leach Tails, was submitted for the preparation of a 30% filled polypropylene composite. A variety of tests then provided comparative data for both the filled and unfilled polypropylene.

The following properties were compared:

- Izod impact strengths
- Flexural moduli
- Tensile properties
- Oxidation induction temperatures
- Heat deflection temperatures
- Melt viscosities and stiffnesses.

The polypropylene resin used was Himont Pro-Fax 6331 homopolymer.

2. EXPERIMENTAL

2.1 Preparation of Filled Compound

Resin/filler mixtures were tumble blended in 1 kg batches with 30% filler by weight.

Compounding was achieved using an Arburg Albrounder 221E/150 injection moulding machine. The blends were moulded at 220°C, then the mouldings cut into small sections and ground into coarse granules using a Wiley mill. The first pass granules were remoulded in the same way once more, and again ground to give a second pass granular compound, ready for test specimen moulding.

Unfilled polypropylene was also put through this two pass treatment to give it the same thermal history.

2.2 Preparation of test Samples

Test specimens were prepared by injection moulding under the following conditions:-

● Plasticizing Cylinder Temperatures	
- Feed Zone	220°C
- Metering Zone	220°C
● Nozzle Percentage Heating	45%
● Injection Hydraulic Pressure	650 psi
● Back Hydraulic Pressure	200 psi

Injection Speed	4 machine units (moderately fast)
Screw Speed	170 rpm
Shot Size	5.75 machine units
Mould Temperature	30°C

2.3 Methods of Testing

2.3.1 Notched Izod impact strengths were measured in accordance with ASTM D256.

2.3.2 Flexural moduli were measured in accordance with ASTM D790, Method I - Procedure A. Specimens measuring 5 inch X 1/2 inch X 1/8 inch were placed on a 2.0 inch support span and tested at a speed of 0.05 inches/minute.

2.3.3 Tensile yield strengths, 1% secant moduli, and ultimate elongations were measured in accordance with ASTM D638. Type I specimens were tested with the aid of strain gauge extensometers, under the following conditions: Speed of testing, 2 inches/minute; gauge length, 2 inches (filled PP), 1 inch (unfilled PP).

2.3.4 Oxidation induction temperatures (OIT) were determined according to ASTM D3350, except specimens were cut using a sharp blade to obtain cross sections through 1/2 inch x 1/8 inch thick moulded bars.

The analysis was carried out using a Dupont 910 Differential Scanning Calorimeter (DSC) and a 9900 programmer.

Copies of the OIT scans can be found in Appendix A.

2.3.5 Heat deflection temperatures were measured in accordance with ASTM D648. Testing was conducted at a 264 psi stress.

2.3.6 Melt viscosities and the storage and loss properties were determined using a Rheometrics RDA-700. Injection moulded bars were used as the test specimens. Sections from the bars were cut and then tested at 189 - 190°C in the frequency sweep mode. Appendix B contains Viscosity (ETA*), storage modulus (G'), and loss modulus (G") curves, plotted against frequency.

3. RESULTS

3.1 Notched Izod Impact Strengths

Impact Strengths (ft-lb/in)

Specimen Number	Unfilled PP	30% Filled PP
1	0.49	0.41
2	0.41	0.41
3	0.41	0.24
4	0.49	0.24
5	0.49	0.33
6	0.41	0.33
7	0.41	0.33
8	0.41	0.24
9	0.41	0.33
10	0.41	0.24
Average	0.43	0.31

3.2 Flexural Moduli

Tangent Flexural Moduli (10^3psi)

Specimen Number	Unfilled PP	30% Filled PP
1	169	275
2	168	272
3	167	271
4	166	267
5	162	265
Average	166	270

3.3 Tensile Properties

	Specimen Number	1% Secant Moduli (10^3psi)	Yield Strengths (psi)	Ultimate Elongations (%)
Unfilled PP	1	199	4830	> 500*
	2	212	4870	> 500*
	3	215	4840	> 500*
	4	214	4780	> 500*
	5	206	4820	> 500*
	Average	209	4830	
30% Filled PP	1	269	3710	3.45
	2	286	3750	3.05
	3	285	3750	3.65
	4	284	3760	4.80
	5	286	3750	3.50
	Average	281	3740	3.69

* Due to machine limitations, elongations beyond 500% could not be measured.

3.4 Oxidation Induction Temperatures

Specimen Number	OIT (°C) Unfilled PP	30% Filled PP
1	218.3	204.8
2	218.3	203.6
Average	218.3	204.2

3.5 Heat Deflection Temperatures

Specimen Number	HDT (°C) Unfilled PP	30% Filled PP
1	52	63
2	54	66
3	58	62
Average	55	64

4. DISCUSSION

The addition of 30% of powder filler to the polypropylene did have an effect on the rheological properties of the resin. The data from Appendix B showed viscosity and moduli had increased. At a frequency of 10 rad/s the following increases occurred: viscosity 16.9%; storage modulus 1.77%; loss modulus 21.7%.

Mechanical properties of moulded specimens were affected to varying degrees.

Impact and tensile yield strengths dropped by approximately 25%. Flexural and tensile moduli increased roughly 60% and 40% respectively. Ultimate elongation was greatly reduced. This is typical behavior for a stiff filler well bonded to the matrix.

Heat deflection temperature (HDT) testing showed the filled sample is more resistant to distortion under load at elevated temperatures. This is consistant with it being stiffer at room temperature.

The OIT results indicated the filled polypropylene was substantially less thermally stable than the unfilled. We speculate that this may have been the result of transition metal ions in the filler catalysing oxidation. A cleanup step, possibly a chelation type stabilizer package should be explored next.

SEM micrographs were taken of the filled mouldings at two stages of their compounding. "Second pass" (see Section 2.1) mouldings, and final specimen mouldings were viewed with attention paid to their fracture surfaces.

The second pass mouldings (hand fractured - Photos #1 and #2) showed reasonably good particle dispersion and bonding to the matrix. The final mouldings (fractured Izod specimens Photos #3 and #4) showed improved dispersion and very good bonding.

The SEM micrographs are presented in Appendix C.

Evaluation of Possible Uses

The behavior of the 30% (weight) filled polypropylene was essentially as expected for any approximately spherical filler at this volume loading. It exhibited normal wet-out on compounding, and moderately good interfacial adhesion to the matrix. The only negative aspect to this material compared to calcium carbonate, for example, was a loss of oxidative stability. This could be corrected at modest costs.

The question of usability being answered in the affirmative, there next arises the question of value. We did observe outgassing, probably of water from specimens we heated. If the material has appropriate pore sizes it might be used as a carrier for liquid additives, such as odorants, insecticides or repellants. Such liquids are generally difficult to add to plastics.

If the binding of water is strong enough, the use of this material in sheet moulding compounds should be explored. Trace amounts of free water introduced by calcium carbonate used in SMC formulations, or by atmospheric contamination, cause adverse changes in application and maturation viscosities. Substitution of a water trapping agent that is chemically inert (unlike CaO presently used) should be evaluated.

Steven K. Haynes
S. Haynes
Project Technologist
Plastics Technology

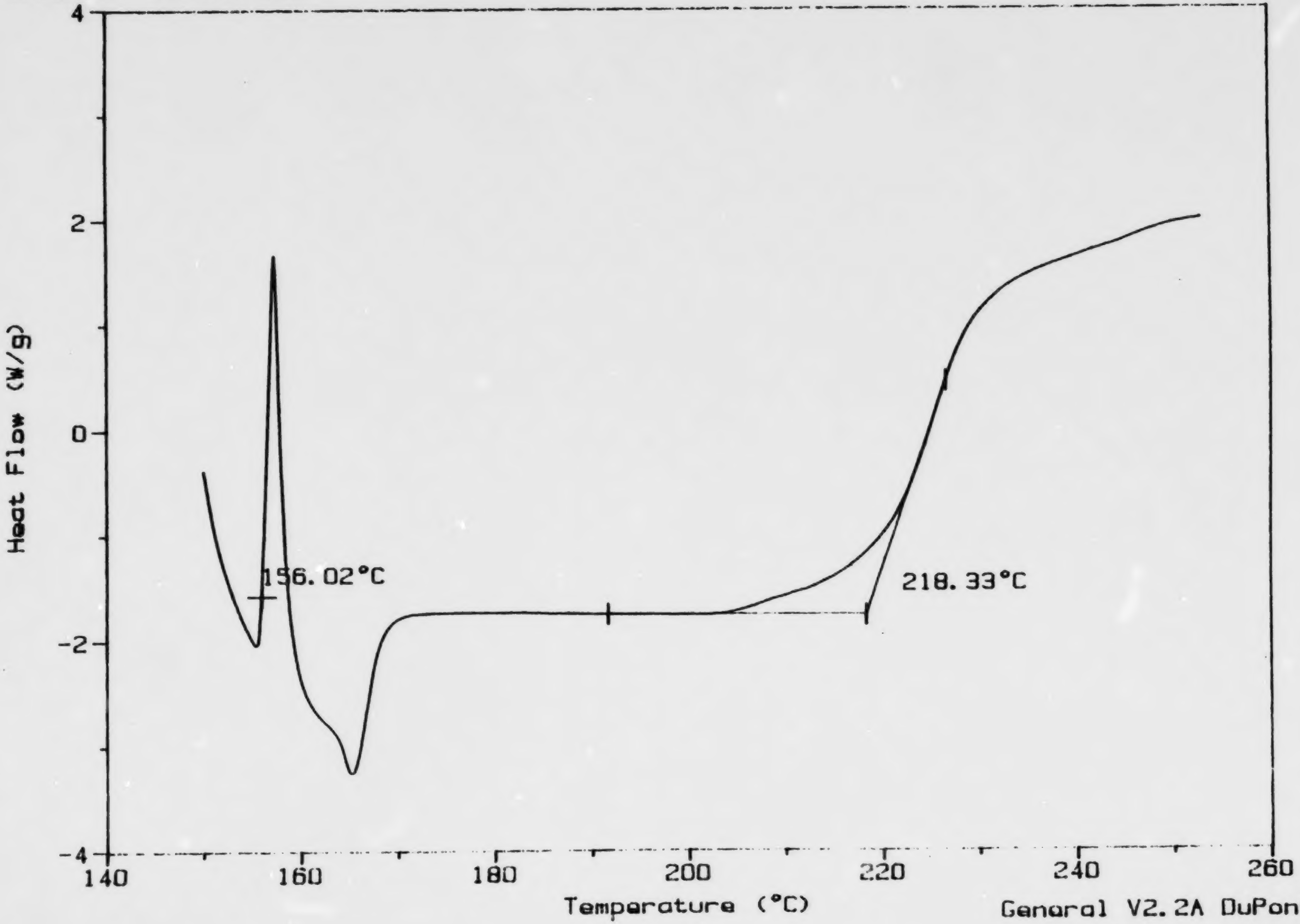
Steve Nazar
S. Nazar
Section Manager
Plastics Technology

APPENDIX A

Sample: POLYPROPYLENE # 1-- .14MM
Size: 2.8000 mg
Method: DSC-ASTM D3350
Comment: ASTM D3350

DSC

File: POLY1.01
Operator: J.E.MCGANN
Run Date: 03/29/88 09:36

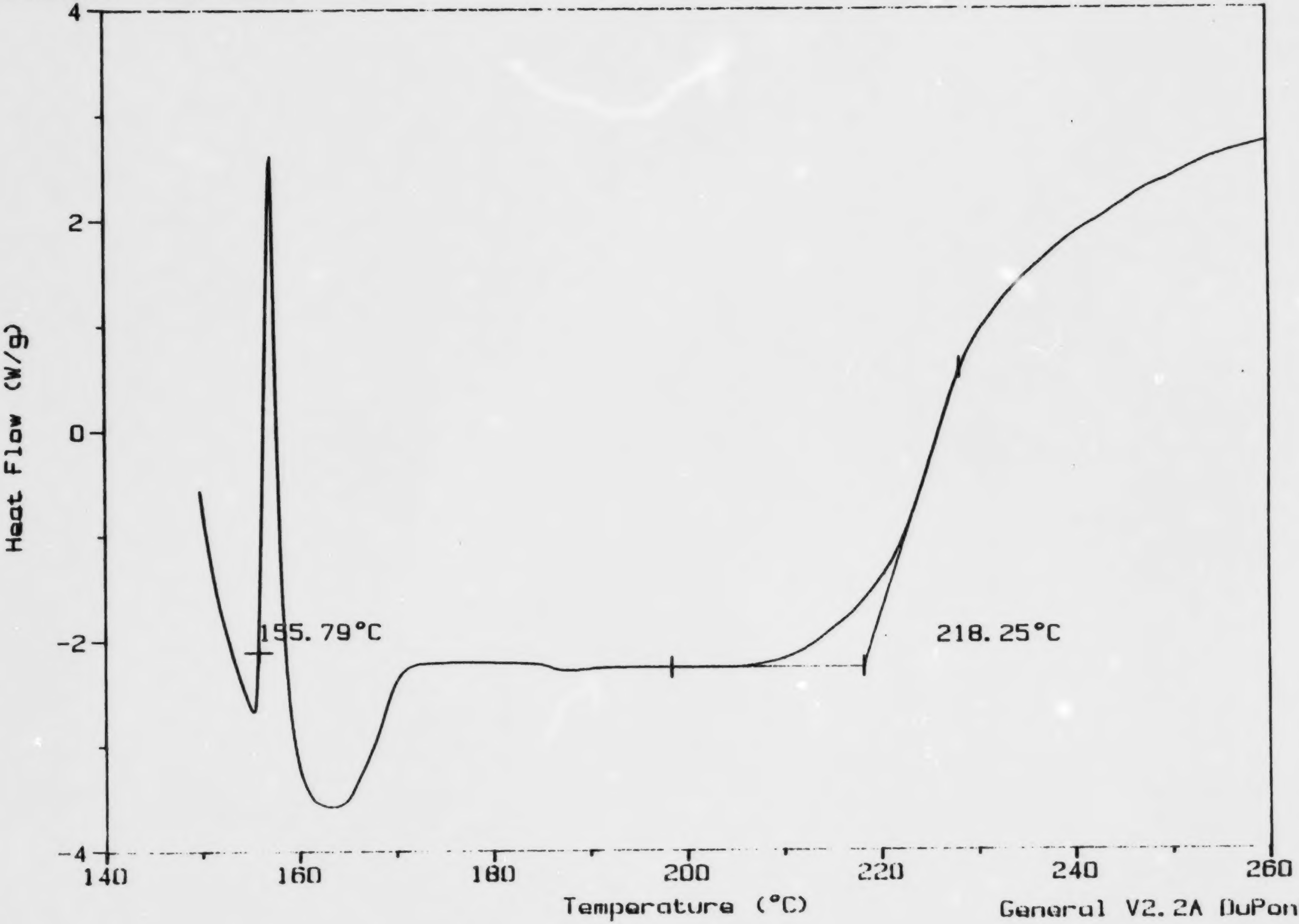


General V2.2A DuPont 9900

Sample: POLYPROPYLENE # 1- .16MM
Size: 2.0000 mg
Method: DSC-ASTM D3350
Comment: ASTM D3350

DSC

File: POLY2.01
Operator: J.E.MCGANN
Run Date: 03/29/88 10:09

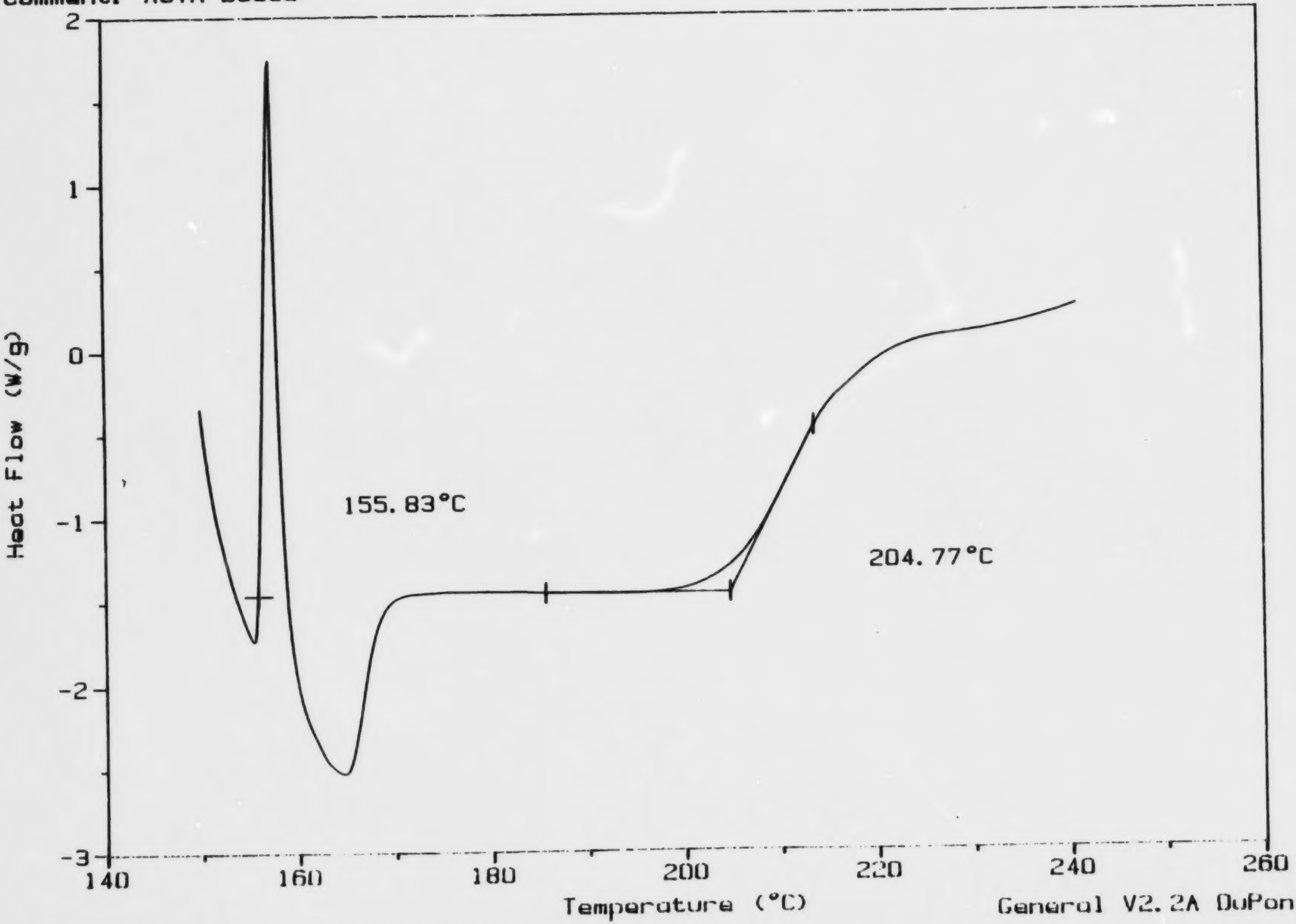


General V2.2A DuPont 9900

Sample: POLYPROPYLENE- FILLED-#1 -.16MM
Size: 3.0000 mg
Method: DSC-ASTM D3350
Comment: ASTM D3350

DSC

File: POLYFILL1.01
Operator: J.E.MCGANN
Run Date: 03/29/88 10:55

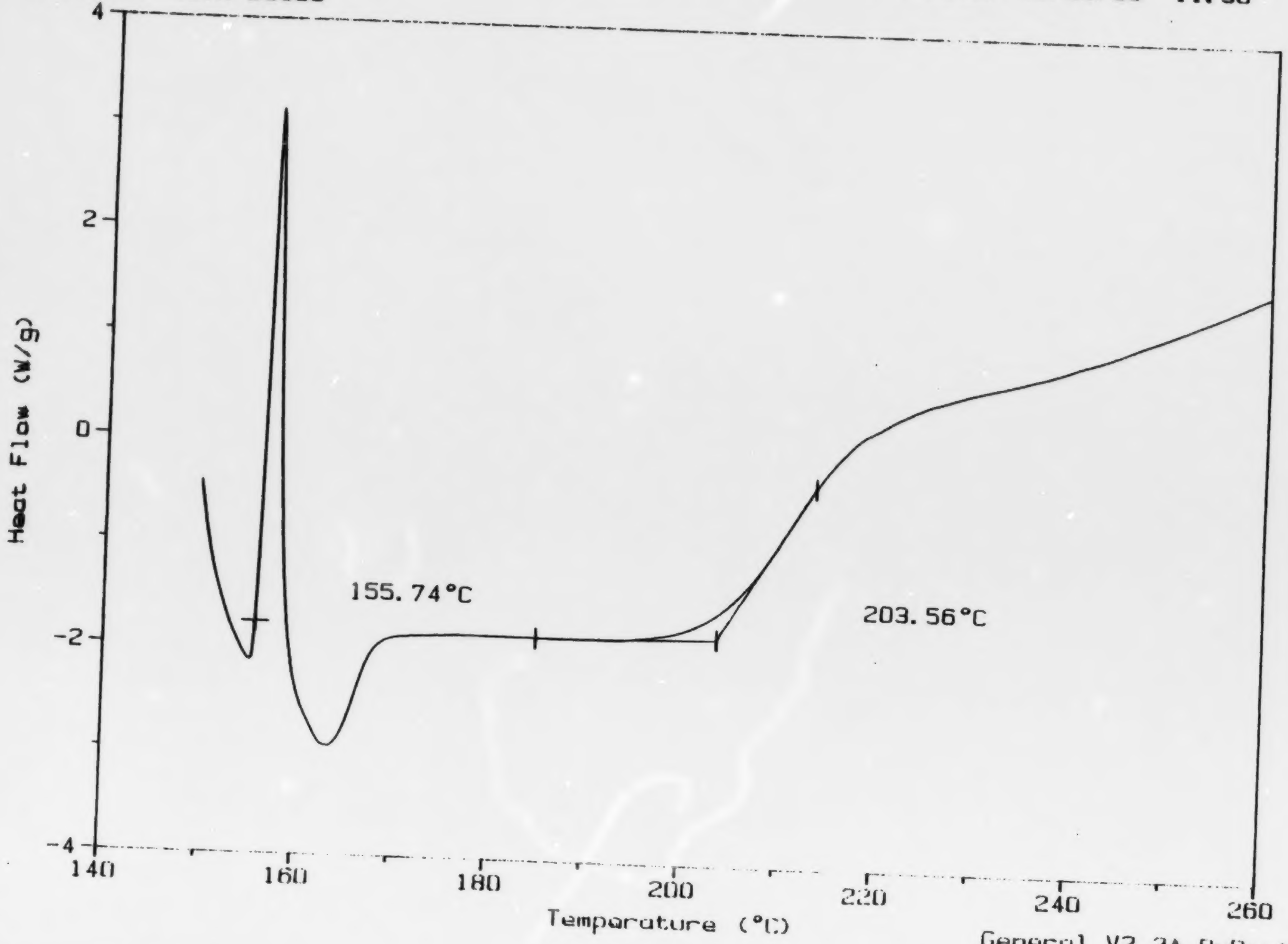


General V2.2A DuPont 990

Sample: POLYPROPYLENE- FILLED-#2 -.15MM
Size: 2.1000 mg
Method: DSC-ASTM D3350
Comment: ASTM D3350

DSC

File: POLYFILL2.01
Operator: J.E.MCGANN
Run Date: 03/29/88 11:30



General V2.2A DuPont 9900

APPENDIX B

```
                        Rheometrics   RECAP II
------------------------------------------------------------------------------
Experiment No. :  17       Sample No. :    1

Title:
POLYPRO UNFILLED FREQUENCY SWEEP AT MELT TEMP.

Operator :POH

Date and Time : Tue 05-Apr-88 - 10:08:39am

Operating Mode :  DYNAMIC

Sweep Type :  2   Frequency Sweep

Geometry :  Disk & Plate

            RADIUS   :     12.500
            GAP      :      2.000


Notes :
```

```
POLYPRO UNFILLED FREQUENCY SWEEP AT MELT TEMP.
------------------------------------------------------------------------------------------
NO.      G'          G"          ETA*         FREQ         TEMP        %STRAIN
         Pa          Pa          Pa.s         rad/s       degrees c
 1   1.547e+01   1.906e+02   1.913e+03   1.000e-01      193.2     9.945e+00
 2   3.074e+01   2.966e+02   2.368e+03   1.259e-01      191.8     9.944e+00
 3   2.757e+01   3.184e+02   2.016e+03   1.585e-01      191.1     9.943e+00
 4   4.361e+01   4.572e+02   2.302e+03   1.995e-01      190.7     9.944e+00
 5   6.749e+01   5.479e+02   2.198e+03   2.512e-01      190.3     9.944e+00
 6   1.134e+02   6.860e+02   2.199e+03   3.162e-01      190.2     9.946e+00
 7   1.451e+02   8.369e+02   2.133e+03   3.981e-01      190.0     9.948e+00
 8   2.039e+02   1.035e+03   2.104e+03   5.012e-01      189.9     9.950e+00
 9   2.622e+02   1.262e+03   2.043e+03   6.309e-01      189.9     9.952e+00
10   3.705e+02   1.538e+03   1.991e+03   7.943e-01      189.8     9.955e+00
11   4.952e+02   1.864e+03   1.929e+03   9.999e-01      189.8     9.960e+00
12   6.563e+02   2.236e+03   1.851e+03   1.259e+00      189.7     9.965e+00
13   8.508e+02   2.692e+03   1.781e+03   1.585e+00      189.6     9.971e+00
14   1.101e+03   3.198e+03   1.655e+03   1.995e+00      189.6     9.978e+00
15   1.424e+03   3.797e+03   1.614e+03   2.512e+00      189.6     9.993e+00
16   1.823e+03   4.483e+03   1.531e+03   3.162e+00      189.6     1.001e+01
17   2.322e+03   5.260e+03   1.445e+03   3.980e+00      189.5     1.002e+01
18   2.918e+03   6.148e+03   1.358e+03   5.011e+00      189.5     1.005e+01
19   3.629e+03   7.126e+03   1.268e+03   6.308e+00      189.5     1.007e+01
20   4.506e+03   8.220e+03   1.180e+03   7.942e+00      189.5     1.010e+01
21   5.527e+03   9.430e+03   1.093e+03   9.998e+00      189.5     1.014e+01
22   6.743e+03   1.076e+04   1.009e+03   1.259e+01      189.5     1.017e+01
23   8.167e+03   1.220e+04   9.262e+02   1.585e+01      189.4     1.020e+01
24   9.786e+03   1.375e+04   8.458e+02   1.995e+01      189.5     1.022e+01
25   1.166e+04   1.541e+04   7.697e+02   2.511e+01      189.4     1.021e+01
26   1.378e+04   1.717e+04   6.964e+02   3.162e+01      189.4     1.017e+01
27   1.619e+04   1.903e+04   6.278e+02   3.980e+01      189.4     1.006e+01
28   1.888e+04   2.099e+04   5.635e+02   5.010e+01      189.4     9.906e+00
29   2.180e+04   2.294e+04   5.017e+02   6.308e+01      189.4     9.704e+00
30   2.509e+04   2.510e+04   4.469e+02   7.941e+01      189.4     9.481e+00
31   2.867e+04   2.729e+04   3.959e+02   9.997e+01      189.4     9.290e+00
32   3.256e+04   2.953e+04   3.492e+02   1.259e+02      189.4     9.116e+00
33   3.674e+04   3.181e+04   3.068e+02   1.584e+02      189.4     9.016e+00
34   4.121e+04   3.417e+04   2.683e+02   1.995e+02      189.4     9.022e+00
35   4.594e+04   3.654e+04   2.338e+02   2.511e+02      189.4     9.126e+00
36   5.086e+04   3.899e+04   2.027e+02   3.161e+02      189.4     9.374e+00
37   5.589e+04   4.150e+04   1.749e+02   3.979e+02      189.4     9.902e+00
38   6.099e+04   4.396e+04   1.504e+02   5.000e+02      189.4     1.058e+01
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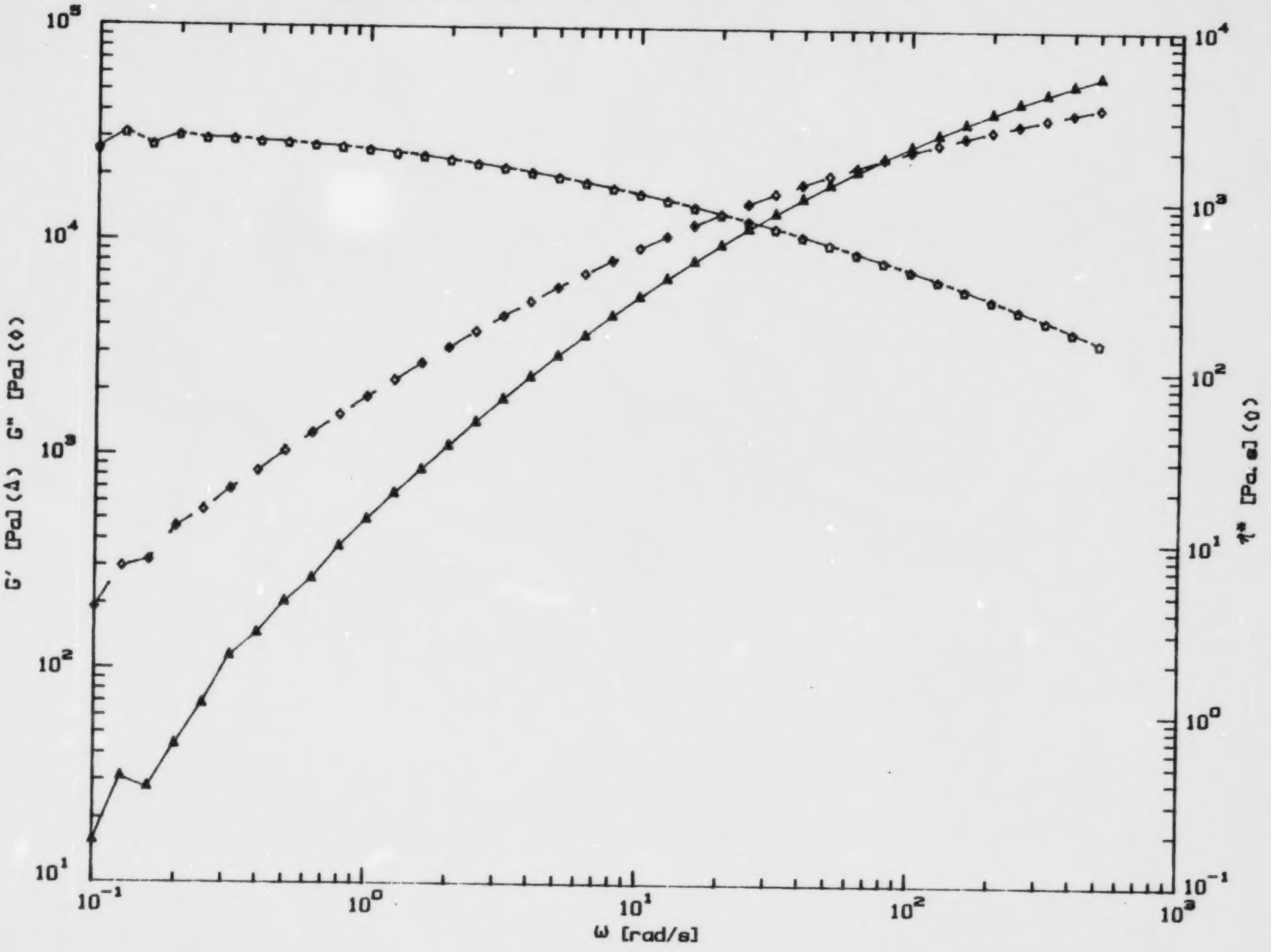
POLYPRO UNFILLED FREQUENCY SWEEP AT MELT TEMP.



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                         Rheometrics   RECAP II
---------------------------------------------------------------------
Experiment No. :   2       Sample No. :   1

Title:
POLYPRO FILLED FREQUENCY SWEEP #2 AT MELT TEMP

Operator :POH

Date and Time : Wed 06-Apr-88 - 10:59:06am

Operating Mode :  DYNAMIC

Sweep Type :  2   Frequency Sweep

Geometry :  Disk & Plate

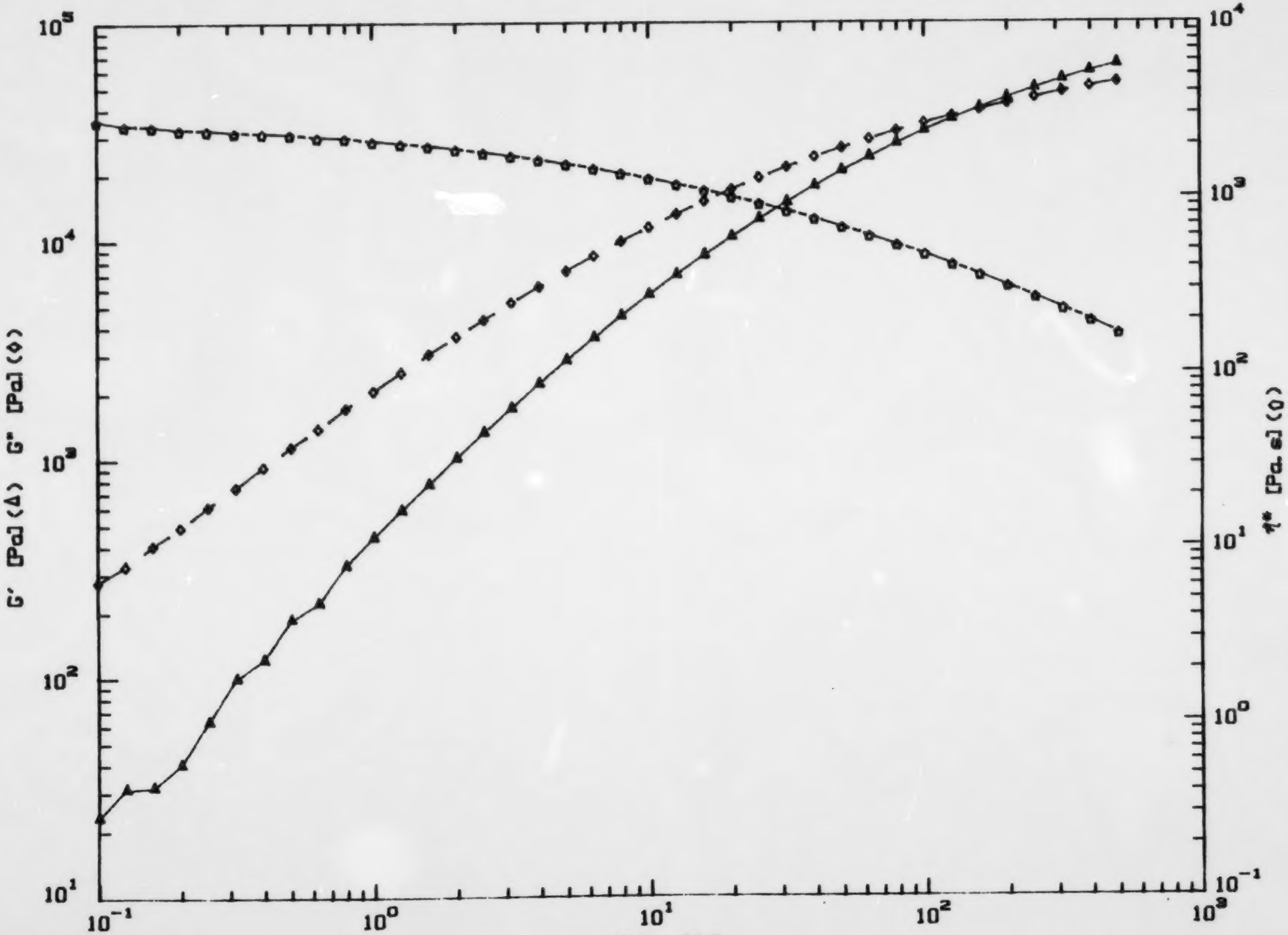
            RADIUS    :     12.500
            GAP       :      2.000


Notes :
SAMPLE WAS DRIED AT 120C OVERNIGHT
NO FOAMING OBSERVED
```

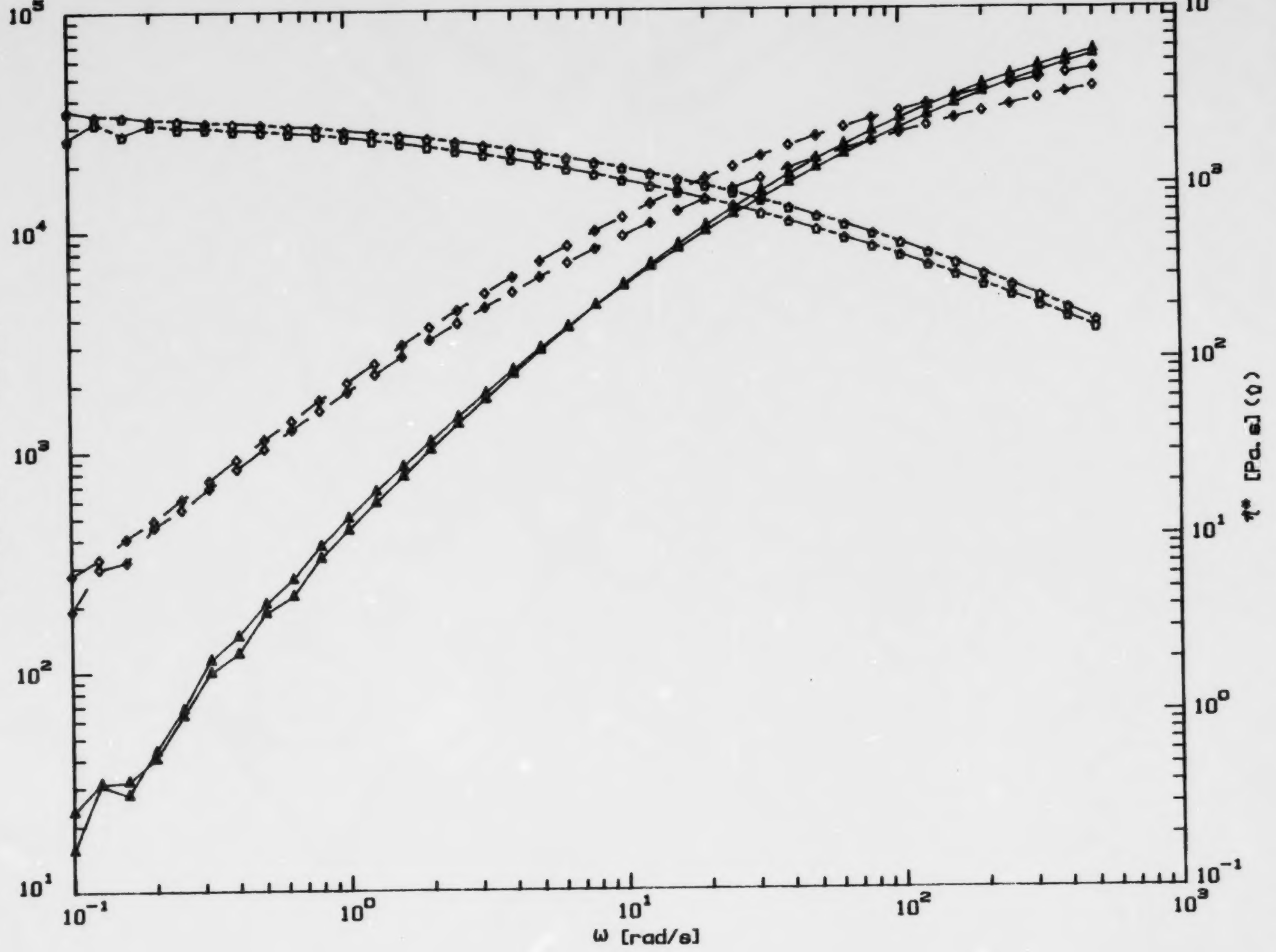
POLYPRO FILLED FREQUENCY SWEEP #2 AT MELT TEMP

NO.	G' Pa	G" Pa	ETA* Pa.s	FREQ rad/s	TEMP degrees c	%STRAIN
1	2.312e+01	2.759e+02	2.769e+03	1.000e-01	188.8	9.943e+00
2	3.122e+01	3.267e+02	2.607e+03	1.259e-01	189.3	9.942e+00
3	3.180e+01	4.059e+02	2.569e+03	1.585e-01	189.4	9.942e+00
4	4.024e+01	4.902e+02	2.465e+03	1.995e-01	189.6	9.943e+00
5	6.299e+01	6.089e+02	2.437e+03	2.512e-01	189.6	9.944e+00
6	9.899e+01	7.417e+02	2.366e+03	3.162e-01	189.7	9.945e+00
7	1.208e+02	9.229e+02	2.338e+03	3.981e-01	189.8	9.947e+00
8	1.848e+02	1.139e+03	2.302e+03	5.012e-01	189.7	9.947e+00
9	2.194e+02	1.381e+03	2.216e+03	6.309e-01	189.8	9.951e+00
10	3.255e+02	1.711e+03	2.193e+03	7.943e-01	189.9	9.954e+00
11	4.374e+02	2.051e+03	2.098e+03	9.999e-01	189.9	9.958e+00
12	5.810e+02	2.497e+03	2.036e+03	1.259e+00	189.9	9.964e+00
13	7.641e+02	3.029e+03	1.971e+03	1.585e+00	189.8	9.970e+00
14	1.010e+03	3.645e+03	1.896e+03	1.995e+00	189.8	9.977e+00
15	1.323e+03	4.352e+03	1.811e+03	2.512e+00	189.9	9.992e+00
16	1.710e+03	5.193e+03	1.729e+03	3.162e+00	189.8	1.001e+01
17	2.213e+03	6.165e+03	1.646e+03	3.980e+00	189.8	1.002e+01
18	2.832e+03	7.259e+03	1.555e+03	5.011e+00	189.8	1.004e+01
19	3.580e+03	8.501e+03	1.462e+03	6.308e+00	189.8	1.007e+01
20	4.514e+03	9.920e+03	1.372e+03	7.942e+00	189.8	1.010e+01
21	5.625e+03	1.148e+04	1.278e+03	9.998e+00	189.8	1.014e+01
22	6.958e+03	1.321e+04	1.186e+03	1.259e+01	189.8	1.017e+01
23	8.535e+03	1.512e+04	1.096e+03	1.585e+01	189.9	1.020e+01
24	1.036e+04	1.714e+04	1.004e+03	1.995e+01	189.9	1.022e+01
25	1.248e+04	1.933e+04	9.163e+02	2.511e+01	189.9	1.022e+01
26	1.489e+04	2.163e+04	8.306e+02	3.162e+01	189.9	1.016e+01
27	1.764e+04	2.407e+04	7.497e+02	3.980e+01	189.9	1.006e+01
28	2.074e+04	2.651e+04	6.720e+02	5.010e+01	189.9	9.893e+00
29	2.401e+04	2.911e+04	5.981e+02	6.308e+01	189.9	9.682e+00
30	2.769e+04	3.174e+04	5.304e+02	7.941e+01	189.9	9.450e+00
31	3.168e+04	3.442e+04	4.679e+02	9.997e+01	189.9	9.233e+00
32	3.587e+04	3.705e+04	4.096e+02	1.259e+02	189.9	9.044e+00
33	4.025e+04	3.967e+04	3.568e+02	1.584e+02	189.9	8.917e+00
34	4.485e+04	4.236e+04	3.092e+02	1.995e+02	189.9	8.896e+00
35	4.960e+04	4.499e+04	2.667e+02	2.511e+02	189.9	8.978e+00
36	5.444e+04	4.784e+04	2.293e+02	3.161e+02	189.9	9.205e+00
37	5.926e+04	5.063e+04	1.959e+02	3.979e+02	189.9	9.682e+00
38	6.380e+04	5.315e+04	1.661e+02	5.000e+02	189.9	1.033e+01

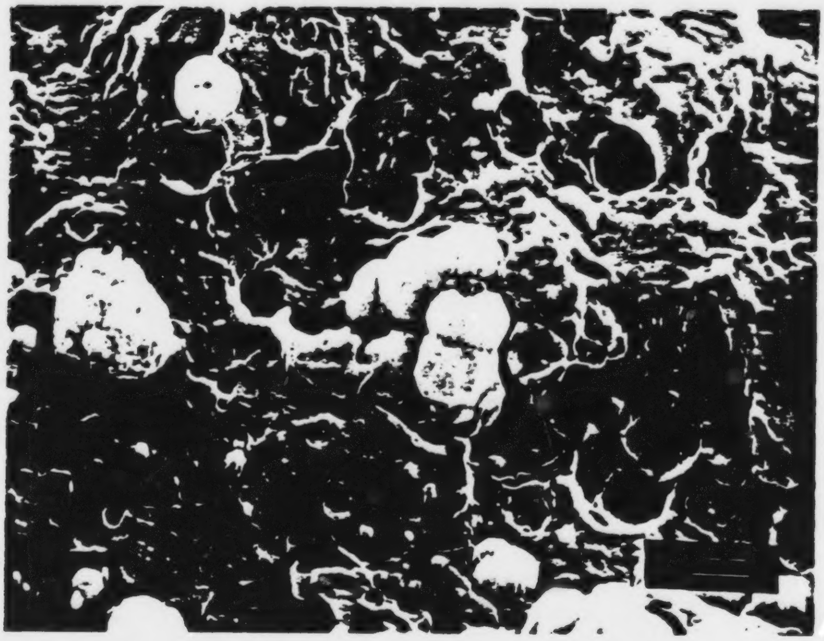
POLYPRO FILLED FREQUENCY SWEEP #2 AT MELT TEMP



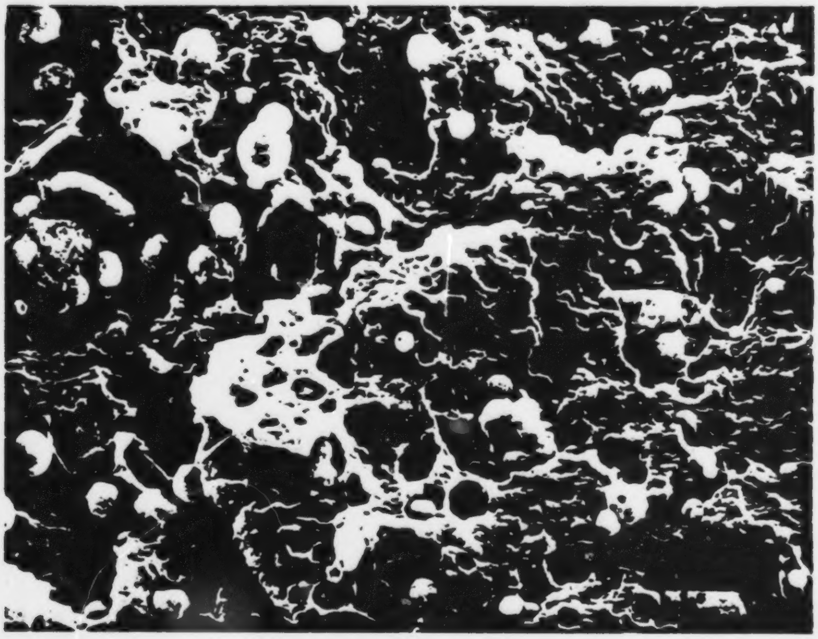
COMPARISON OF UNFILLED PP TO 30% FILLED PP



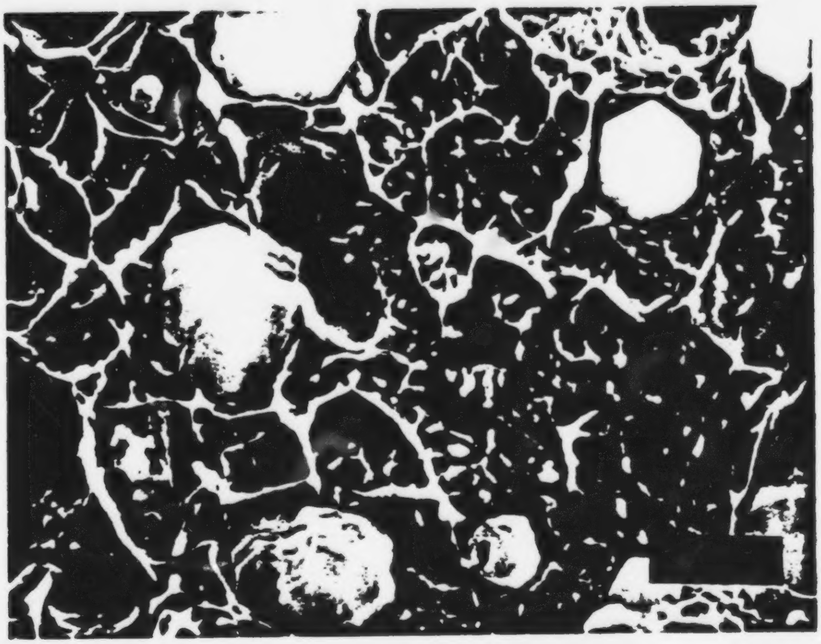
APPENDIX C



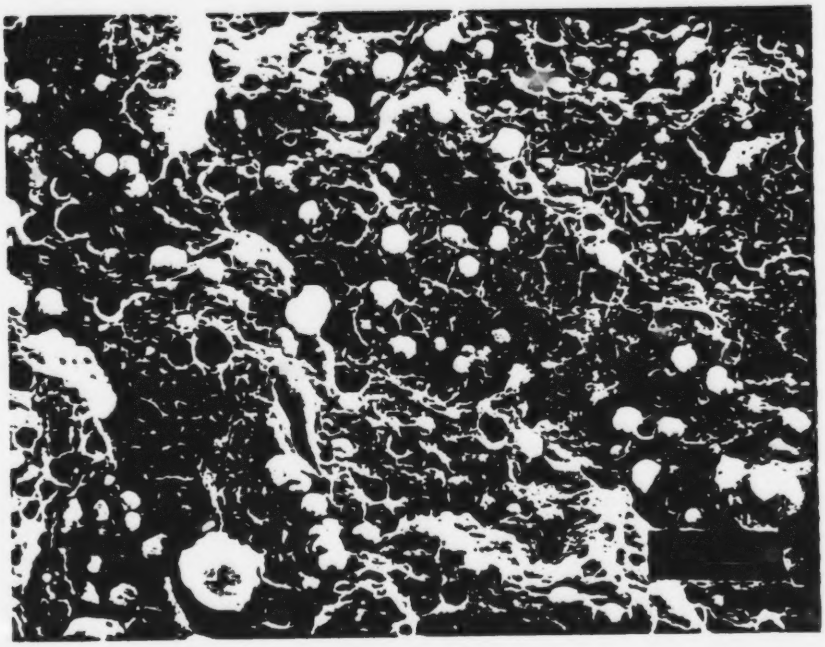
Photograph 1



Photograph 2



Photograph 3



Photograph 4

APPENDIX IV DETERGENT TESTING

Carbovan Inc.
Fabrication of FCC Catalysts from Suncor Flyash Leach Residue
ORF Account No. 41-10874

Detergent Testing Report

1. Standard test procedures for zeolites in detergent formulations are commonly found in the literature. The tests are basically simple in nature and are initially based on testing the uptake of dissolved calcium and magnesium from standard water solutions. Providing the zeolite complies with this basic test and meets all other specifications, detergent formulation and ultimately the cleaning performance of the final detergent can thus be monitored.

Test Procedure

The procedure consists of formulating a standard tap water of known Ca^{++} and Mg^{++} ion concentration. The concentrations of Ca^{++} and Mg^{++} should approach that expected in the area of use. Two standard solutions were tested. Solution A with 40 mg/L Ca^{++} 8.4 mg/L Mg^{++} and solution B 16.0 mg/L Ca^{++} and 5.2 mg/L Mg.

The decrease in water hardness is measured as a function of zeolite contact time, the temperature during contact and the concentration of zeolite present. Washing conditions were simulated by carrying out determinations at room temperature. Solids concentrations varied from 0.03g - 0.09 g per 100 mls. solution. Aliquots of the solution were taken at 1 minute, 5 minute and 10 minute intervals after the initial slurrying. The samples were filtered and filtrate analysed by atomic absorbtion spectroscopy for Ca and Mg ion concentration.

The tests were repeated for both the material under test as well as a standard commercial Zeolite A used in detergent formulations.

The zeolite under test is then reported as having a maximum equivalent calcium ion capacity, which is reported as mg Ca^{++}/gram zeolite.

The zeolite material tested was caustic leach tailings from a 3:1 ESP/BHA feed, while the standard was Ethyl Zeolite A manufactured by Ethyl Corporation, U.S.A.

In Tables 1 and 2 (Standard Water 16 ppm Ca^{++} 5.2 ppm Mg^{++}) and Tables 3 and 4 (Standard Water 40 ppm Ca^{++} 8.4 ppm Mg ++), it is evidently clear that at room temperature and acceptable zeolite concentration levels there is extremely poor uptake of Ca^{++} and Mg^{++} ions by the leach tailings in comparison to commercial grade Zeolite A.

Leach tails, at the highest solids additions still only achieved 10 mg Ca^{++}/g and 1 mg Mg^{++}/g. This compares to specifications of at least 200 mg Ca^{++}/g solids for the commercial grade Zeolite A. The Ethyl Zeolite A showed 100% take up of Ca ion with moderate take up of the Mg^{++} ion. The solution head sample do not contain enough dissolved Ca^{++} ion to establish the maximum that this material would reach.

It is quite evident that further testing of leach tail material for detergent application would be of little consequence taking into account the poor comparison this material has with other specifications listed in Section 3.

CARBOVAN
CONTACT TEST (Ca and Mg)

ROOM TEMP
TABLE 1

Sample	Volume (ml) Mixture of Standard	Amount of Leach Tails	Temp (C) Std. of sol.	Contact Time	Analysis in ppm Ca	Analysis in ppm Mg	Solids ion uptake Ca mg/g solids	Solids ion uptake Mg mg/g solids
Head Sample Water					16	5.2	0.0	0.0
Z-1-A	100 ml	0.03 g	23 C	1 min	17	5.3	0.0	0.0
Z-2-A	100 ml	0.03 g	22.5 C	5 min	17	5.3	0.0	0.0
Z-3-A	100 ml	0.03 g	22.5 C	10 min	17	5.3	0.0	0.0
Z-4-A	100 ml	0.06 g	22.5 C	1 min	17	5.1	0.0	0.2
Z-5-A	100 ml	0.06 g	22.5 C	5 min	16	5.0	0.0	0.3
Z-6-A	100 ml	0.06 g	22.5 C	10 min	17	5.1	0.0	0.2
Z-7-A	100 ml	0.09 g	22.5 C	1 min	16	4.9	0.0	0.3
Z-8-A	100 ml	0.09 g	22.5 C	5 min	16	4.8	0.0	0.4
Z-9-A	100 ml	0.09 g	22.5 C	10 min	17	4.9	0.0	0.3

TABLE 2

Sample	Volume (ml) Mixture of Standard	Amount of Ethyl Zeolite "A"	Temp (C) Std. of sol.	Contact Time	Analysis in ppm Ca	Analysis in ppm Mg	Solids ion uptake Ca mg/g solids	Solids ion uptake Mg mg/g solids
Head Sample Water					16	5.2	0.0	0.0
Z-1-D	100 ml	0.03 g	18.5 C	1 min	8.4	5.1	35.3	0.3
Z-2-D	100 ml	0.03 g	18.5 C	5 min	3.2	5	42.6	0.6
Z-3-D	100 ml	0.03 g	19.0 C	10 min	0.9	4.8	50.0	1.3
Z-4-D	100 ml	0.06 g	20.0 C	1 min	1.1	4.6	24.8	1.3
Z-5-D	100 ml	0.06 g	19.5 C	5 min	0.1	4.8	26.5	0.6
Z-6-D	100 ml	0.06 g	20.0 C	10 min	0.1	4.5	26.5	1.2
Z-7-D	100 ml	0.09 g	19.0 C	1 min	0.1	4.5	17.6	0.8
Z-8-D	100 ml	0.09 g	19.5 C	5 min	0.3	3.4	17.4	2.0
Z-9-D	100 ml	0.09 g	20.0 C	10 min	0.1	3.5	17.6	1.9

CARBOVAN
CONTACT TEST (Ca and Mg)

TABLE 3

Sample	Tap Water Volume (ml)	Amount of Leach Tails	Temp (C) of sol. (C)	Contact Time	Analysis in ppm Ca	Analysis in ppm Mg	Solids ion uptake Ca mg/g solids	Solids ion uptake Mg mg/g solids
Head Sample Water	--	--	--	--	40	8.4	0.0	0.0
Z-1-F	100 ml	0.03 g	20 C	1 min	38	8.1	6.0	1.0
Z-2-F	100 ml	0.03 g	23 C	5 min	40	8.3	0.0	0.0
Z-3-F	100 ml	0.03 g	21 C	10 min	37	8.1	10.0	1.0
Z-4-F	100 ml	0.06 g	22.5 C	1 min	38	8.1	3.0	1.0
Z-5-F	100 ml	0.06 g	22.5 C	5 min	34	8.3	10.0	0.0
Z-6-F	100 ml	0.06 g	22.5 C	10 min	38	8.2	2.0	0.3
Z-7-F	100 ml	0.09 g	21.5 C	1 min	38	8.1	2.0	0.2
Z-8-F	100 ml	0.09 g	22. C	5 min	40	8.1	0.0	0.3
Z-9-F	100 ml	0.09 g	22. C	10 min	39	7.9	1.0	0.4

TABLE 4

Sample	Tap Water Volume (ml)	Amount of Ethyl Zeolite A used (g)	Temp (C) of sol. (C)	Contact Time	Analysis in ppm Ca	Analysis in ppm Mg	Solids ion uptake Ca mg/g solids	Solids ion uptake Mg mg/g solids
Head Sample Water					40	8.4	0.0	0.0
Z-1-E	100 ml	0.03 g	21.5 C	1 min	27	8.3	43.0	0.3
Z-2-E	100 ml	0.03 g	22 C	5 min	22	8.4	60.0	0.0
Z-3-E	100 ml	0.03 g	21.5 C	10 min	19	8.2	70.0	0.3
Z-4-E	100 ml	0.06 g	21.5 C	1 min	16	8.1	26.0	0.5
Z-5-E	100 ml	0.06 g	21.5 C	5 min	6.1	8.4	56.5	0.0
Z-6-E	100 ml	0.06 g	22 C	10 min	2.4	8.2	62.6	0.3
Z-7-E	100 ml	0.09 g	21 C	1 min	11	8.4	32.2	0.0
Z-8-E	100 ml	0.09 g	22. C	5 min	1	7.5	43.0	1.0
Z-9-E	100 ml	0.09 g	22. C	10 min	1.5	6.4	43.0	2.2

APPENDIX V PROGRESS REPORTS

Fabrication of FCC Catalysts from Suncor Flyash Leach Residue For Carbovan Inc.

Progress Report #1

Carbovan Inc.
2200 Argentia Road
Mississauga, Ontario
L5N 2K7

Attn: Mr. Nairn McQueen

Fabrication of FCC Catalysts from Suncor Flyash Leach Residue For Carbovan Inc.

Progress Report #1

Carbovan Inc.
2200 Argentia Road
Mississauga, Ontario
L5N 2K7

Attn: Mr. Nairn McQueen

Submitted by:

V. I. Lakshmanan
C. A. Booth
G. M. Freeman
Mineral Resources

ORF Account No. 41-10874
DSS Contract Serial No. 23440-7-9124/01-SQ

November 19, 1987

Fabrication of FCC Catalysts from Suncor Flyash Leach Residue
For Carbovan Inc.

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1. PRELIMINARY CHARACTERIZATION OF CARBOVAN LEACH RESIDUE - ORF EVALUATION

Ontario Research Foundation at the request of Carbovan Inc. conducted bench and pilot scale test work to recover vanadium from flyash products at Suncor Tarsands Plant, Fort McMurray.

The flowsheet developed to recover vanadium included leaching, solution treatment and vanadium product recovery. During the bench scale flow sheet development studied attempts were made to enhance the leach recovery by minimising potential vanadium losses to leached residue. Possible exchange of dissolved vanadium to leached residue or post precipitation of vanadium compounds were considered.

To identify such losses leach residues were examined by XRD, and SEM/EDX techniques. Such tests did not indicate discrete presense of vanadium compounds.

However residues obtained at two different leach conditions, on XRD examinations revealed the following (Appendix 1).

i) Leach tails obtained with (Na_2CO_3 + NaOH).

Analcime	$NaAlSi_2O_6H_2O$	Approx. 90%
Zeolite	$Na_3Al_3Si_5O_{16}$ $6H_2O$	Approx. 5%
Unidentified Compounds		Approx. 5%

ii) Leach Tails obtained with NaOH

Analcime	Approx. 20%
Zeolite	Approx. 75%
Unidentified Compounds	Approx. 5%

It is known to those familiar with zeolite, that they have potential applications in the use as FCC Catalysts, molecular sieves, detergents, ion exchanger and fillers. During the test program conducted on behalf of Carbovan Inc., ORF had requested Dr. S. Ranganathan of Saskatchewan Research Council to evaluate the potential use of Carbovan Leach residue for application as FCC Catalyst.

2. PRELIMINARY EVALUATION OF CARBOVAN LEACH RESIDUE FOR CATALYST TESTING - SRC STUDY

Saskatchewan Research Council conducted fluid cracking catalyst potential by microactivity test (FCC MAT). The test procedure was based upon ASTM D 3907-80 FCC MAT procedure. One deviation that was included during the tests included two test temperatures 482°C and 504°C.

The results of the tests are as follows.

	Sample	Description*	Reaction T °C	Conversion (Wt %)	Volume (ml)
1	No. 1	As received	482	43.1	40
2	No. 1	Decoked	482	20.7	11
3	No. 2	Dried	482	41.1	97
4	No. 2	Dried	504	47.7	109
5	No. 2	Diluted with Sand	482	61.0	62
6	No. 3	As received	482	40.0	64

* Sample 1, dry leach residue, Sample 2, wet leach residue, Sample 3, retreated leach residue.

The feed stock used for all tests was a gas oil received from a conventional light crude typically used in Canadian refineries.

During typical FCC Catalyst tests the catalyst is first decoked in a furnace at 590°C for 3 hours. Hence some of carbovan residue was decoked and compared to as received material and found it to have higher activity without decoking. Remaining tests were done without decoking.

Carbovan leach residue had smaller particle size compared to commercial catalysts (approximately 70 um). Small particle size can cause problems with MAT unit because the catalyst will pack during the test and gas oil may not be exposed to sufficient catalytic surface. Higher than normal pressure drops were indicated showing bed packing. However Test No. 5, when diluted with sand significantly improved conversion to 61%.

Commercial catalysts under similar test conditions convert approximately 60-70% gas-oil to gasoline. Gas make was found to be high and was considered due to some dehydrogenation, requiring possible further developmental work. The results indicated potential for carbovan leach residue to act as catalyst. When diluted with sand conversion rates were comparable to clays (Betonite) and slightly less than available commercial catalysts (Appendix II).

3. NEW CHARACTERIZATION WORK IN PROGRESS AT ORF

The (NaOH) and (NaOH + Na_2CO_3) leach residues, are submitted for following analysis.

i) XRD

ii) SEM

iii) Surface area

iv) Particle size distribution

v) Multi elemental chemical analysis.

The particle size distribution results are shown in Appendix III. These will be discussed upon completion of the remaining analysis.

4. FRESH ESP, BH FLYASH SAMPLES CHARACTERIZATION

Representative samples of ESP and BH Suncor ash have been decarbonized by separating carbon by flotation. Varsol and MIBC were used as flotation agent. The decarbonized ash samples are submitted for following analysis.

i) Size distribution

ii) S.E.M.

5 representative ESP and BH ASA feed samples are submitted for the following analysis:

1. X.R.D.

2. Multi elemental analysis

iii) S.E.M.

The particle size distribution results are shown in Appendix III. These will be discussed upon completion of the remaining analysis.

Gm Freeman

V. I. Lakshmanan
Project Manager
Mineral Resources

G. M. Freeman
Operations Manager
Mineral Resources

APPENDIX I: XRD Examinations

MEMO

ONTARIO**RESEARCH**
FOUNDATION

SHERIDAN PARK RESEARCH COMMUNITY
MISSISSAUGA ONTARIO CANADA L5K 1B3 • (416) 822-4111 • TELEX 06-982311

December 13, 1985

TO: Dr. V.I. Lakshmanan

FROM: E. Niskanen

REF: Renzy 41-10476A, Work Order 1282

Subject: X-Ray Diffraction Analysis of Extraction Residues.

Report: X85291

Two extraction residues have been examined by x-ray diffraction to determine the presence of small amounts of calcium vanadate.

The XRD patterns obtained from both samples consisted of numerous intense peaks, making it difficult to detect without interference the weak peaks expected from the calcium vanadates. However, after examining the XRD patterns carefully, we have found no positive evidence to suggest that calcium metavanadate ($CaVO_3$) or calcium pyrovanadate ($Ca_2V_2O_7$) is present in either of the residues. Under the present circumstances it is expected that these vanadates would have to be present as well-crystallized compounds in concentrations exceeding about 2% by weight before they could be detected.

Attacned are copies of tne XRD patterns on which the expected positions for the strongest peaks of calcium metavanadate (MV) and calcium pyrovanadate (PV) are marked.

The following information was obtained on the identification of the major crystalline phases in the two residues.

Sample marked "Na_2CO_3"

Analcime	$NaAlSi_2O_6.H_2O$	-	approx.	90%
Zeolite	$Na_3Al_3Si_5O_{16}.6H_2O$	-	"	5%
unidentified components		-	"	5%

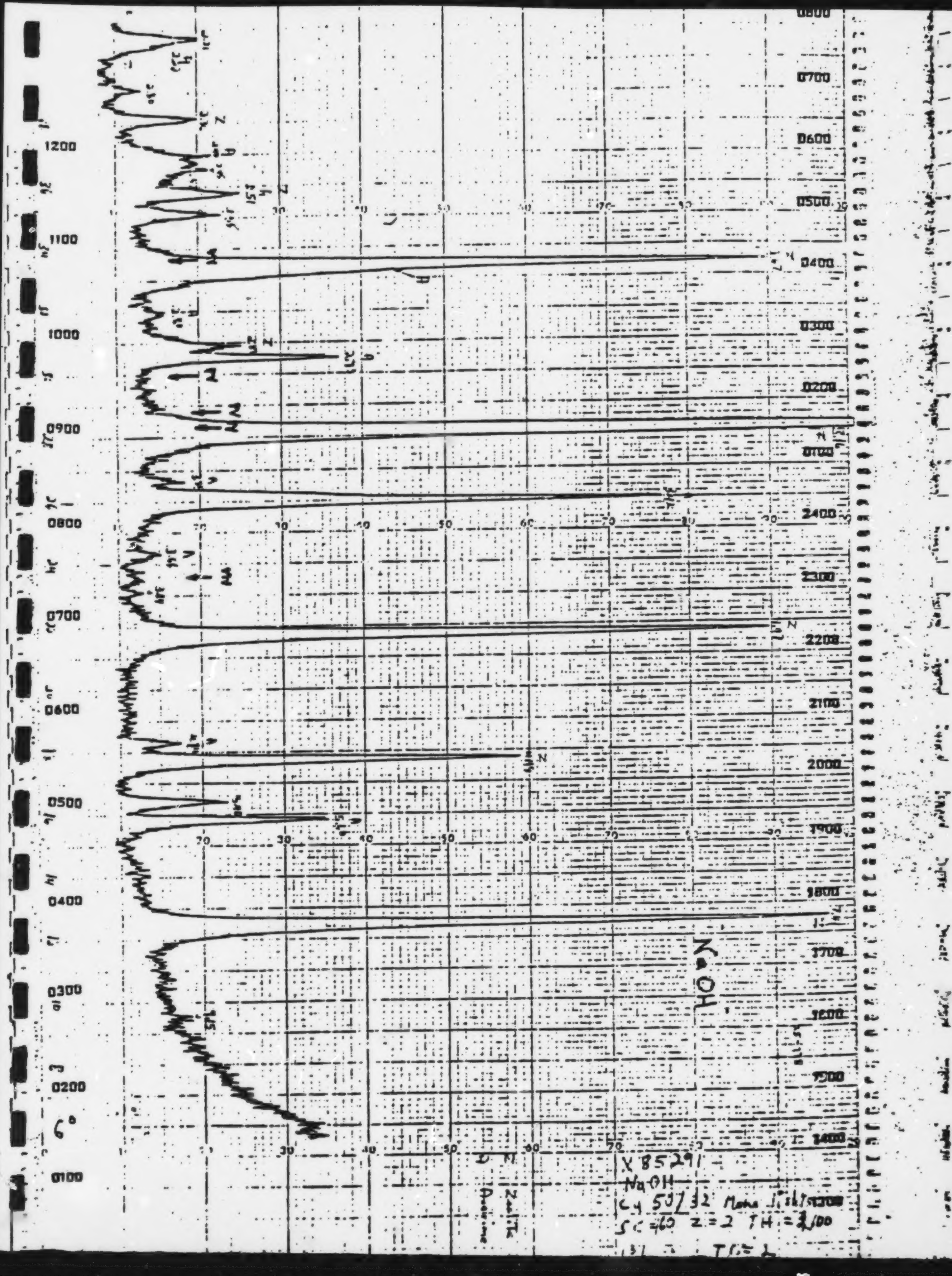
Sample marked "NaOH"

Analcime	-	approx.	20%
Zeolite	-	approx.	75%
unidentified components	-	approx.	5%

E. Niskanen

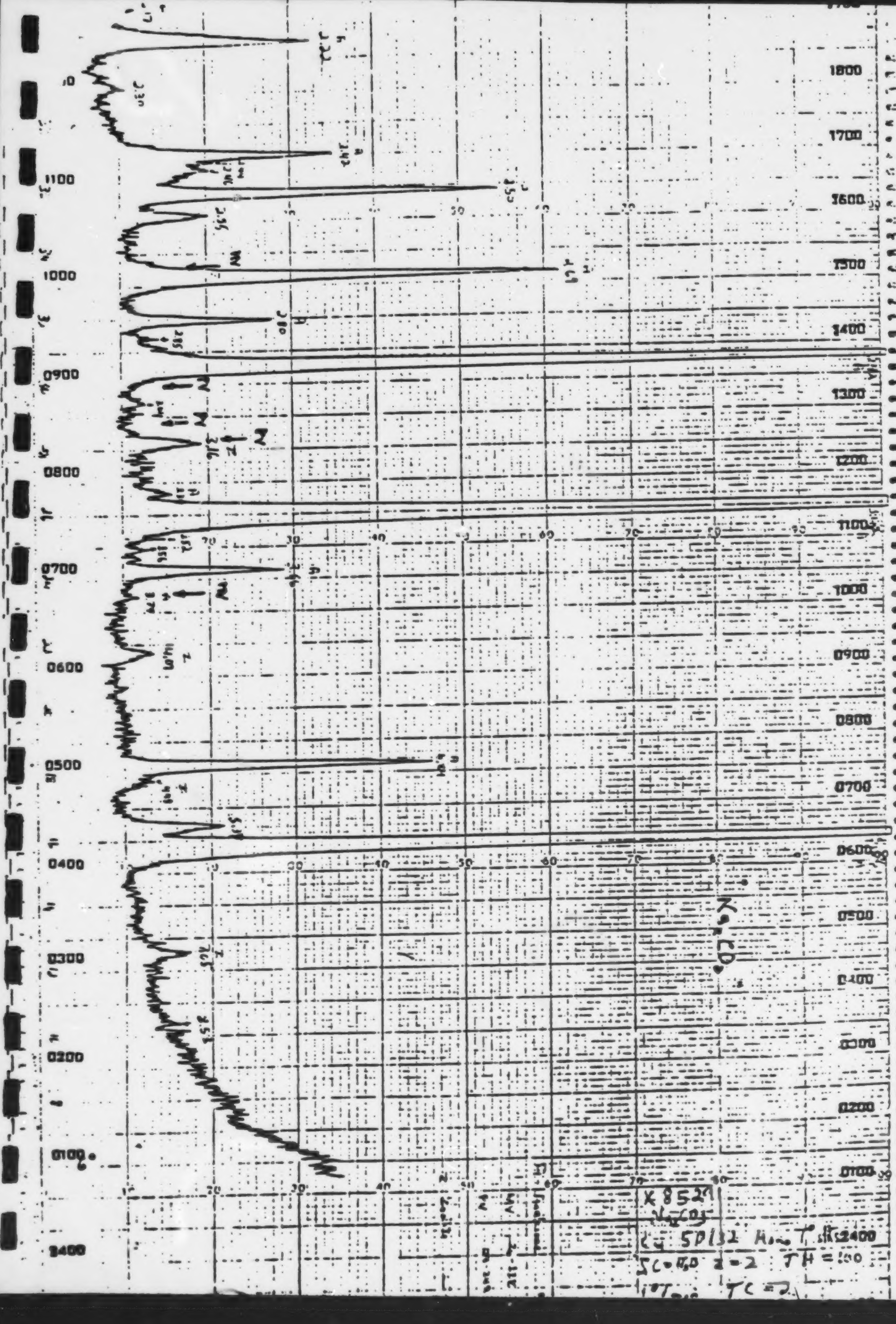
E. Niskanen, P. Eng.
Consultant
Materials Characterization Centre

EN/sj



NaOH

X 85291
NaOH
C4 50/32 Mono
SC=60 Z=2 TH=2/100
TC=2



Na_2CO_3

X 852
Na_2CO_3
SP132
SC = 4.0
TH = 100
TC = 2

APPENDIX II: Zeolite Material for Catalyst Testing

M1.7.3

PETROLEUM DIVISION

SRC
Saskatchewan
Research Council 515 Henderson Drive Regina. Sask Canada S4N 5X1 Phone. (306) 787-9400 Telecopy 949-2644

FAX 787 8811

March 26, 1986

Dr. V.I. Lakshmanan
Manager, Mineral Processing and Hydrometallurgy Groups
Ontario Research Foundation
Sheridan Park Research Community
Mississauga, Ontario
L5K 5X1

Dear Dr. Lakshmanan:

Re: Zeolite Material for Catalyst Testing

As we discussed on the telephone, SRC has completed the testing of the zeolite material to determine its suitability as a catalyst. With this letter I will provide additional information regarding the details of the testing, the results and the conclusions that can be interpreted from the results.

The catalyst test is called Fluid Cracking Catalysts by Microactivity Test (FCC MAT). The apparatus used is a MAT unit. A schematic of the equipment is provided. Not shown on the diagram is the gas collection and analysis equipment. The procedure we use is based on the ASTM D 3907-80 FCC MAT procedure which is also enclosed. The only deviation from the ASTM procedure is that we often use a variety of reaction temperatures (in this case we used two 482°C and 504°C).

The purpose of the test is to measure the conversion of the gas oil feedstock (boiling range 345-525°C) to gasoline (material boiling less than 216°C). Other factors sometimes measured are the coke factor (the amount of material polymerized to coke) and gas factor (amount of gas made, includes hydrogen and hydrocarbons C_4 and lighter). The coke and gas factor are measures of the catalyst's selectivity and are not that important at this stage.

. . 2

We received three samples of zeolite material from ORF. The only difference between the first two was that the second sample had not been dried. The third sample had been treated a second time at ORF. The following table summarizes the results of our MAT tests.

MAT TEST RESULTS

Sample Description	Reaction T °C	Conversion (wt.%)	Volume (ml)
Gas			
1. No. 1, as received	482	43.4	40
2. No. 1, decoked	482	20.7	11
3. No. 2, dryed	482	41.1	97
4. No. 2, dryed	504	47.7	109
5. No. 2, diluted with sand	~~482~~ 504	61.0	62 →
6. No. 3, as received	482	40.0	64

The feedstock used for all cases was a gas oil derived from a conventional light crude typically used at Canadian refineries at this time.

A number of relevant observations were made when the tests were performed. For a typical FCC catalyst test the catalyst must first be decoked in a furnace at 590°C for 3 hours. We decoked some of the catalyst and compared it to the as received material and found it to have a higher activity without decoking. All the remaining tests were done without decoking. Although the first sample appeared dry it still contained a significant amount of water. Initially we thought we had achieved high conversion until the water settled out of the reaction products. All three samples provided similar conversions when tested as received although there is a variation in the gas volume.

[redacted] or these samples it was significantly less. Small particle size can cause problems with the MAT unit because the catalyst will pack during the test and the gas oil may not be exposed to sufficient catalytic surface. Higher than normal pressure drops were observed during the experiments indicating some bed packing. For one test we diluted the catalyst with some sand and the conversion improved dramatically to 61%. We have tested the sand by itself to determine if it has any catalytic capability. I will forward these results to you when they are complete.

. . 3

Synthetic

→ Different gas oil

Under similar test conditions a commercial catalyst will convert approximately 60-70% of the gas oil to gasoline. From a conversion point of view this zeolite material has significant potential. However, gas make is quite high, 40-50 mls of gas are normally produced when testing a commerical catalyst. We performed one gas analysis (of the last experiment) and found that the gas was mainly hydrogen. The H_2/CH_4 ratio was approximately three, whereas for a commercial catalyst the ratio is 0.5-1.0. This indicates that some dehydrogenation of the product is occurring, which is not desirable. This problem could be overcome with some additional development work on the zeolite.

The results indicate that there is potential for developing this material into a catalyst. When diluted with the sand it provided conversions similar to natural clays (bentonite) and slightly less than available commercial catalysts. We are willing to provide suggestions into possible improvements should your client wish to pursue development.

If there are any questions regarding the tests, please do not hesitate to contact me at (306)787-9331.

Yours truly,

D Soveran

Douglas W. Soveran
Senior Research Engineer

DS/dh

c.c. R. Ranganathan
E. Ogu

Attachments

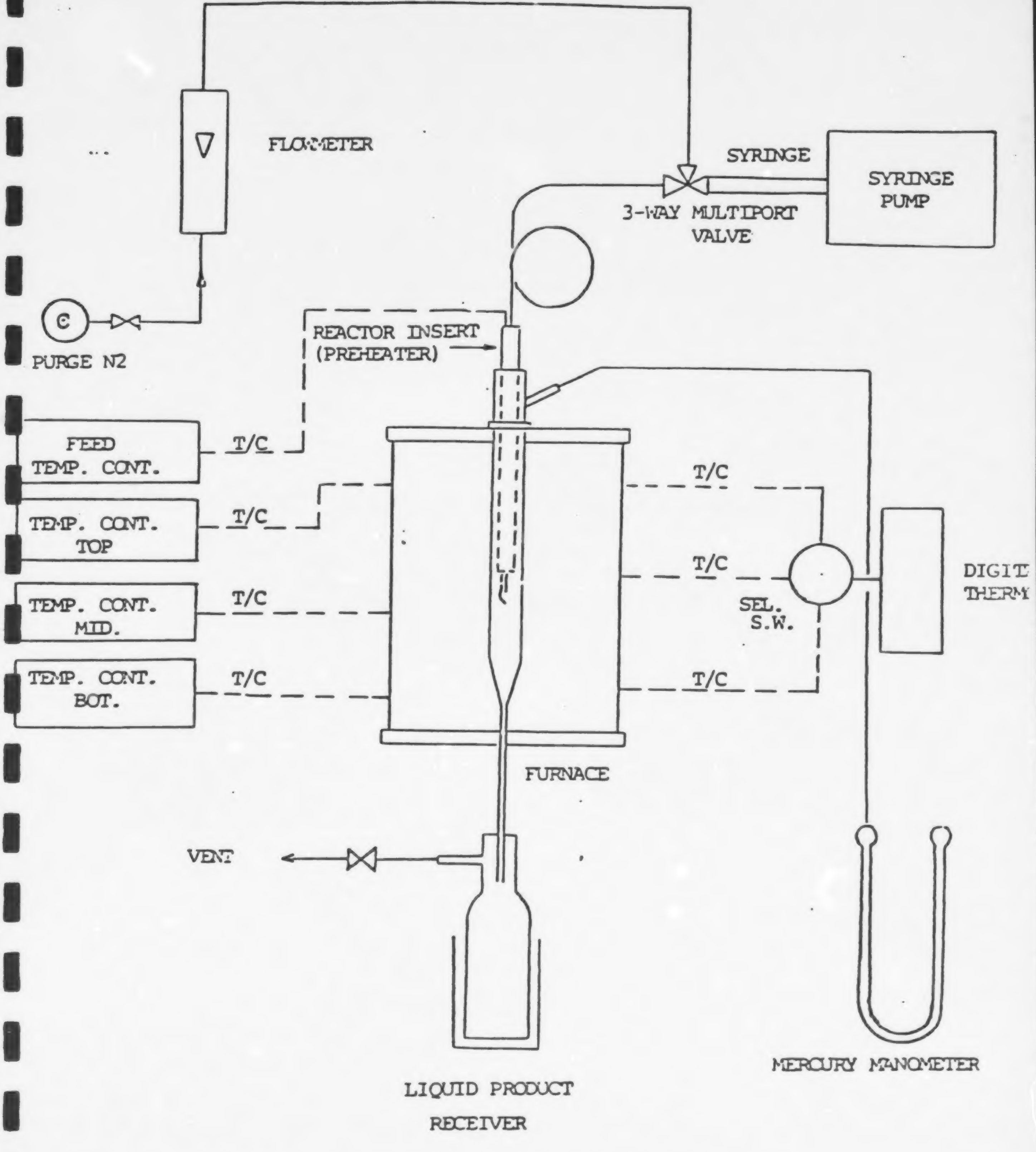

FLOWMETER
SYRINGE
SYRINGE PUMP
3-WAY MULTIPORT VALVE
REACTOR INSERT (PREHEATER)
C
PURGE N2
FEED TEMP. CONT.
T/C
TEMP. CONT. TOP
T/C
TEMP. CONT. MID.
T/C
TEMP. CONT. BOT.
T/C
T/C
T/C
T/C
SEL. S.W.
DIGIT THERM
FURNACE
VENT
LIQUID PRODUCT RECEIVER
MERCURY MANOMETER

FIGURE 1 - MICROACTIVITY FLOW CHART

Note: This drawing not to scale.

The gas oil samples solidified easily at room temperature. Prior to use in each experimental run, the feed sample was placed in an oven and heated for approximately 10 minutes at 40°C. This simple procedure made it possible to transfer the gas oil into a syringe.

2 Reactor Preparation

Before each experimental run, the reactor was properly rinsed with acetone and dried in air. The reactor feed line as well as the product receiver were prepared in a like manner. The essence was to rid the reactor components of contaminants that might affect the experimental results. While the reactor was being prepared, the furnace was preheated to 482°C (900°F) to establish a steady and stable temperature before inserting the reactor into the furnace. A plug of borosilicate glass wool was inserted into the reactor to serve as the catalyst support. Four grams of the decoked equilibrium catalyst were measured and added in a free flowing manner into the reactor. Following the addition of the catalyst, the reactor was tapped slightly to ensure good radial distribution and another plug of glass wool was positioned above it. The amount of the catalyst required was determined by first establishing the weight of an empty crucible and adding the catalyst to increase this weight by 4 grams. Usually, about 0.03 grams of excess catalyst was added to compensate for any catalyst lost to the surface of the crucible.

3 EXPERIMENTAL PROCEDURE

1 Sample Preparation

The best overall performance of any catalyst used in an FCC operation can be assessed by knowledge of its activity. Activity measures the ability of the catalyst to convert gas oil. Spent or equilibrium catalysts from refinery FCC operations have very limited activity and are continuously regenerated by decoking, i.e. burning off the coke components in the air.

The equilibrium catalysts used in this study were sequentially decoked prior to use. The decoking procedure closely followed the method stipulated by ASTM D3907-80. A shallow bed of the equilibrium catalyst sample in a porcelain crucible was placed in a muffle furnace and heated as follows:

120°±20°C (250°±40°F) for 1 hour,
120°C (250°F) to 590°C (1094°F) for approximately 1 hour,
590°±20°C (1094°±40°F) for 3 hours.

After the five hour decoking period, the catalyst sample was fully regenerated as indicated by its whitish colour. The hot crucible containing the decoked catalyst sample was placed in a desiccator to prevent moisture pickup.

After ensuring the tip of the insert thermocouple was bent directly under the tip of the reactor feed tubing, the insert (preheater) was placed into the reactor. This necessary step ensured proper measurement of gas oil preheat temperature. The position of the reactor feed tube insert above the catalyst bed was adjusted to 10-50 mm. This adjustment prevented the insert thermocouple from touching the catalyst bed thereby ensuring that the catalyst bed temperature was not monitored in favour of the feed temperature.

The reactor, so prepared, was placed in the preheated furnace. The nitrogen feed line was connected to the reactor via the 3-way multiport valve and the reactor purged with 30 ml/min of nitrogen for 30 minutes. Purging the reactor prior to the addition of oil helped to stabilize the reactor temperature. Following the insertion of the reactor into the furnace, the electrical connection on the integral oil feed was made as well as connecting the feed preheat thermocouple.

3 Preparation of Syringe and Liquid Product Receiver

The 10 ml. syringe was filled with the gas oil sample and its weight determined. The nitrogen feed line was temporarily disconnected to enable the gas oil syringe to be connected to the 3-way multiport valve. The syringe thermocouple was placed on the syringe body which was heated to 40°±5°C by a heat lamp. The heat lamp was switched on and off depending on whether the syringe temperature was steady at 40°C or not. A wet ice bath was prepared and installed for the liquid product receiver. This receiver was embedded in the cold bath and connected to a vent or a gas sampling bag depending on the need.

4 Run Conditions

Each experimental run was carried out when the reactor temperature had stabilized at 482°C (900°F). The syringe pump was set to deliver 1.3 grams of the gas oil feed in 75 seconds. When the syringe and reactor temperatures were respectively 40°C and 482°C, the multiport valve was switched from the nitrogen flow to the gas oil feed position. The syringe pump was started to transfer 1.3 grams of the oil feed in 75 seconds. This transfer time was determined using a stop watch. Immediately following the gas oil transfer into the reactor, the nitrogen flow was restarted and the reactor as well as the product receiver purged with 30 ml/min of nitrogen for 15 minutes. This purging was necessary to flush into the product receiver any cracked hydrocarbon fractions trapped in the catalyst bed.

At the end of the nitrogen purge, the liquid product receiver was disconnected from the reactor, sealed, dried and weighed immediately. The liquid product hold-up at the exit port of the reactor was collected by means of a Q-tip and its weight determined. (This substance is regarded as unconverted material and is taken into account when calculating the weight percent conversion of the gas oil).

The amount of the liquid product was determined and then analyzed by.

gas chromatography using a simulated distillation technique. The essence was to determine the weight percent of hydrocarbons boiling above 216°C. This was subsequently used to calculate the overall measured conversion. A summary of the analytical results is presented in Table 2.

The activity of the equilibrium catalyst used in each calibration experiment was evaluated on the basis of weight percent conversion of the gas oil in the microactivity test (MAT) unit. The weight percent conversion was determined using the following measured conversion formula:

$$\text{Measured conversion, wt\%} = \frac{F - \frac{R \times L}{100} - H}{F} \times 100$$

where:

F = grams of gas oil fed into the reactor

R = weight percent of material boiling above 216°C in liquid product receiver

L = grams of liquid product in receiver

H = grams of liquid hold-up at reactor exit line.

A summary of the results compiled from the measured conversion is shown in Table 2.

APPENDIX III: Particle Size Distribution Results

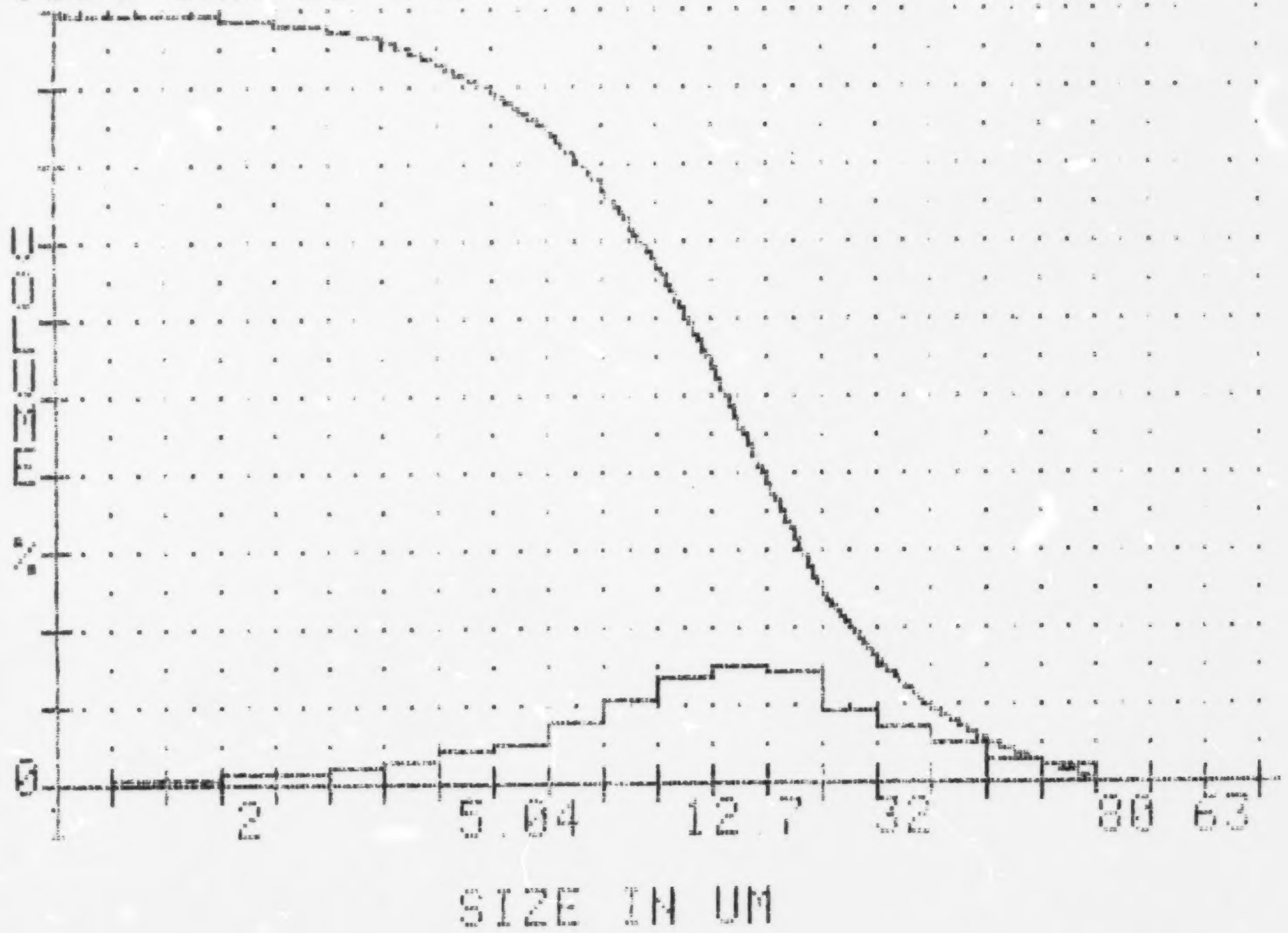
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

```
DATE: [redacted]
SAMPLE: J3239        BHA Float Tails
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#    SIZE            DIFF       CUM
                        VOL %      VOL %
****************************************
1       1               0          100
2       1.26            .38        100
3       1.59            .48        99.62
4       2               .83        99.13
5       2.52            1.03       98.3
6       3.17            1.51       97.28
7       4               2.28       95.77
8       5.04            3.65       93.49
9       6.35            4.97       89.84
10      8               7.44       84.87
11      10.08           10.3       77.44
12      12.7            13.11      67.14
13      16              14.92      54.02
14      20.16           14.25      39.11
15      25.4            9.24       24.86
16      32              6.69       15.62
17      40.32           4.34       8.93
18      50.8            2.74       4.6
19      64              1.86       1.86
20      80.63           0          0
21      101.59          0          0
22      128             0          0

****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                   16.07 UM
MEDIAN:                 17.03 UM
MODE                    18.94 UM
STANDARD DEVIATION:     2.05 UM
COEF. VAR.:             12.77 %
SKEWNESS:               .83 NEGATIVE
KURTOSIS:               2.54 PLATYKURTIC
```

100% SAMPLE: J3239 BHA FLOAT TAILS



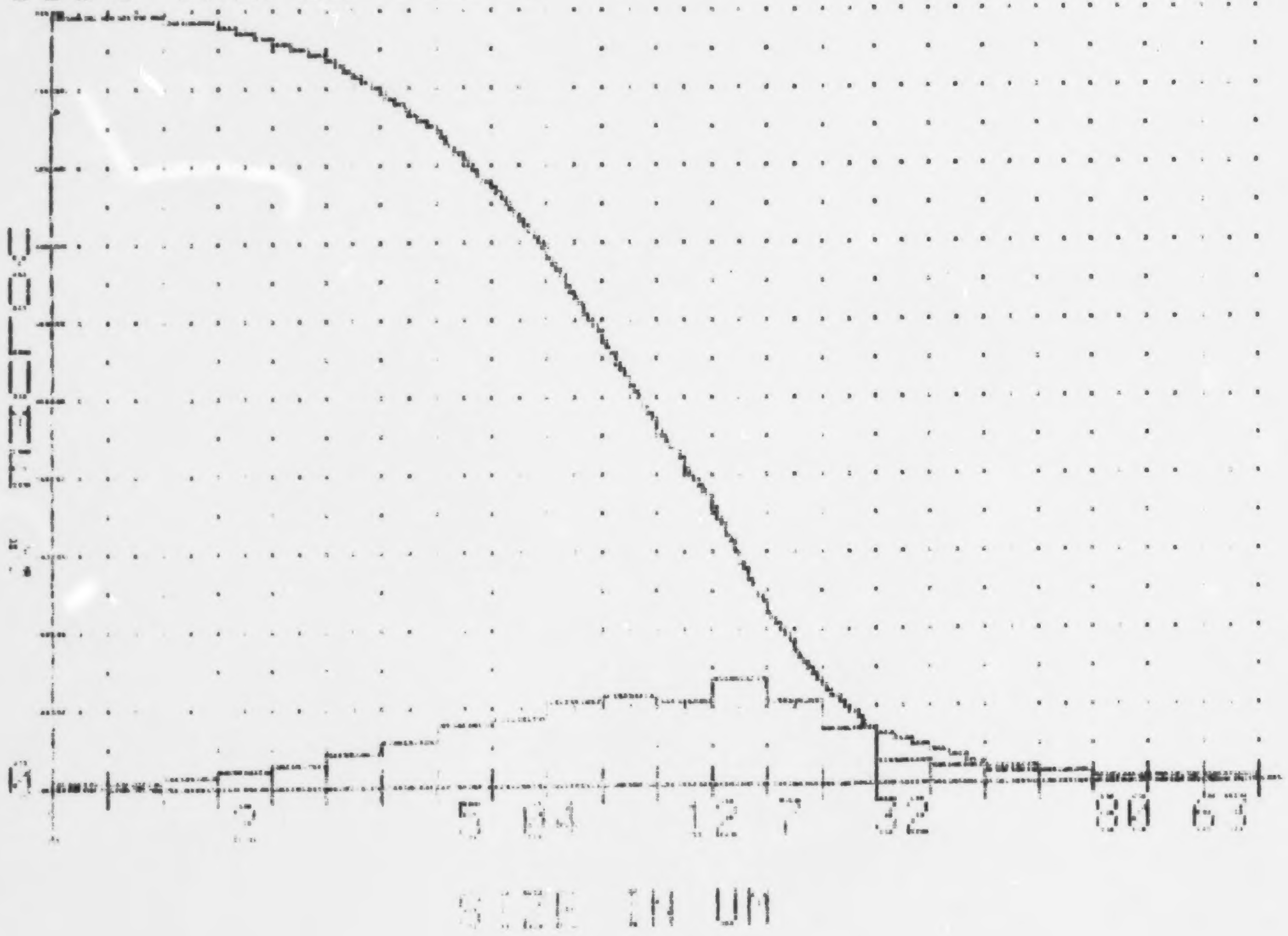
```
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

DATE: NOV 13 87
SAMPLE: J3240   ESP FLOAT TAILS
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#    SIZE            DIFF        CUM
                        VOL %       VOL %
****************************************
1       1               .49         100
2       1.26            .49         99.51
3       1.59            .93         99.02
4       2               1.83        98.09
5       2.52            2.62        96.26
6       3.17            3.72        93.63
7       4               5.41        89.92
8       5.04            7.32        84.51
9       6.35            8.52        77.19
10      8               10.65       68.67
11      10.08           11.26       58.01
12      12.7            10.76       46.76
13      16              13.17       35.99
14      20.16           10.22       22.82
15      25.4            6.52        12.61
16      32              2.26        6.09
17      40.32           2.14        3.83
18      50.8            .89         1.69
19      64              .8          .8
20      80.63           0           0
21      101.59          0           0
22      128             0           0


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                    11.19 UM
MEDIAN:                  11.88 UM
MODE                     17.75 UM
STANDARD DEVIATION:      2.16 UM
COEF. VAR.:              19.29 %
SKEWNESS:                .86 NEGATIVE
KURTOSIS:                2.81 PLATYKURTIC
```

100% SAMPLE: J3240 ESP FLOAT TAILS

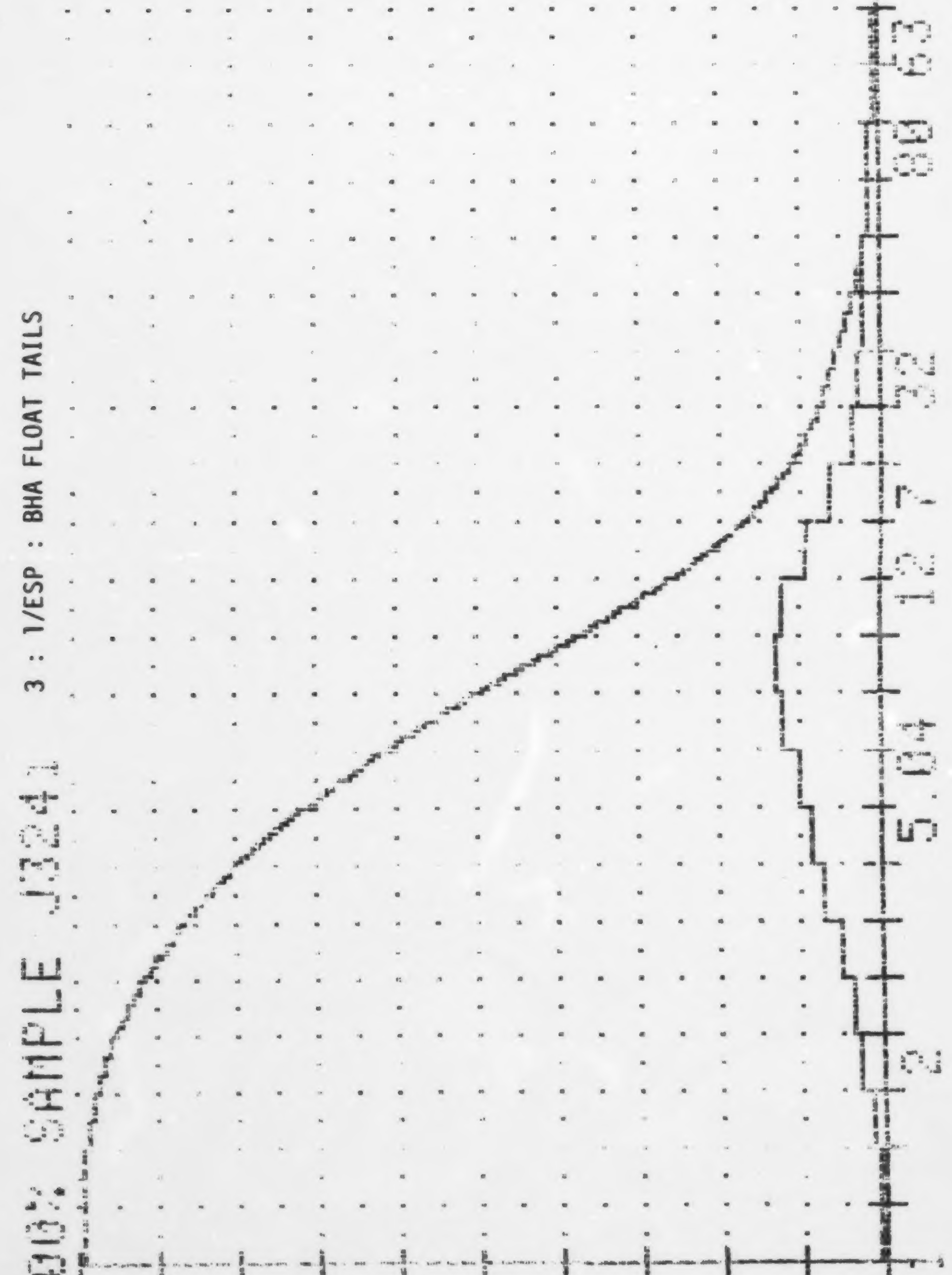


```
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

DATE: NOV 13 87
SAMPLE: J3241    3:1/ESP: BHA FLOAT TAILS
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#    SIZE            DIFF        CUM
                        VOL %       VOL %
****************************************
1       1               .57         100
2       1.26            .65         99.43
3       1.59            1.22        98.78
4       2               2.45        97.55
5       2.52            3.42        95.1
6       3.17            4.84        91.69
7       4               6.8         86.85
8       5.04            8.62        80.05
9       6.35            9.79        71.42
10      8               11.9        61.63
11      10.08           12.75       49.73
12      12.7            11.61       36.98
13      16              9.05        25.37
14      20.16           5.92        16.32
15      25.4            3.4         10.4
16      32              2.66        7
17      40.32           2.03        4.34
18      50.8            1.56        2.31
19      64              0           .75
20      80.63           .75         .75
21      101.59          0           0
22      128             0           0


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                     9.77 UM
MEDIAN:                   10.03 UM
MODE                      11.13 UM
STANDARD DEVIATION:       2.21 UM
COEF. VAR.:               22.65 %
SKEWNESS:                 1 NEGATIVE
KURTOSIS:                 3.35 LEPTOKURTIC
```


100% SAMPLE J3241
3 : 1/ESP : BHA FLOAT TAILS
VOLUME
%
0
2
5.04
12.7
32
80
63
SIZE IN UM

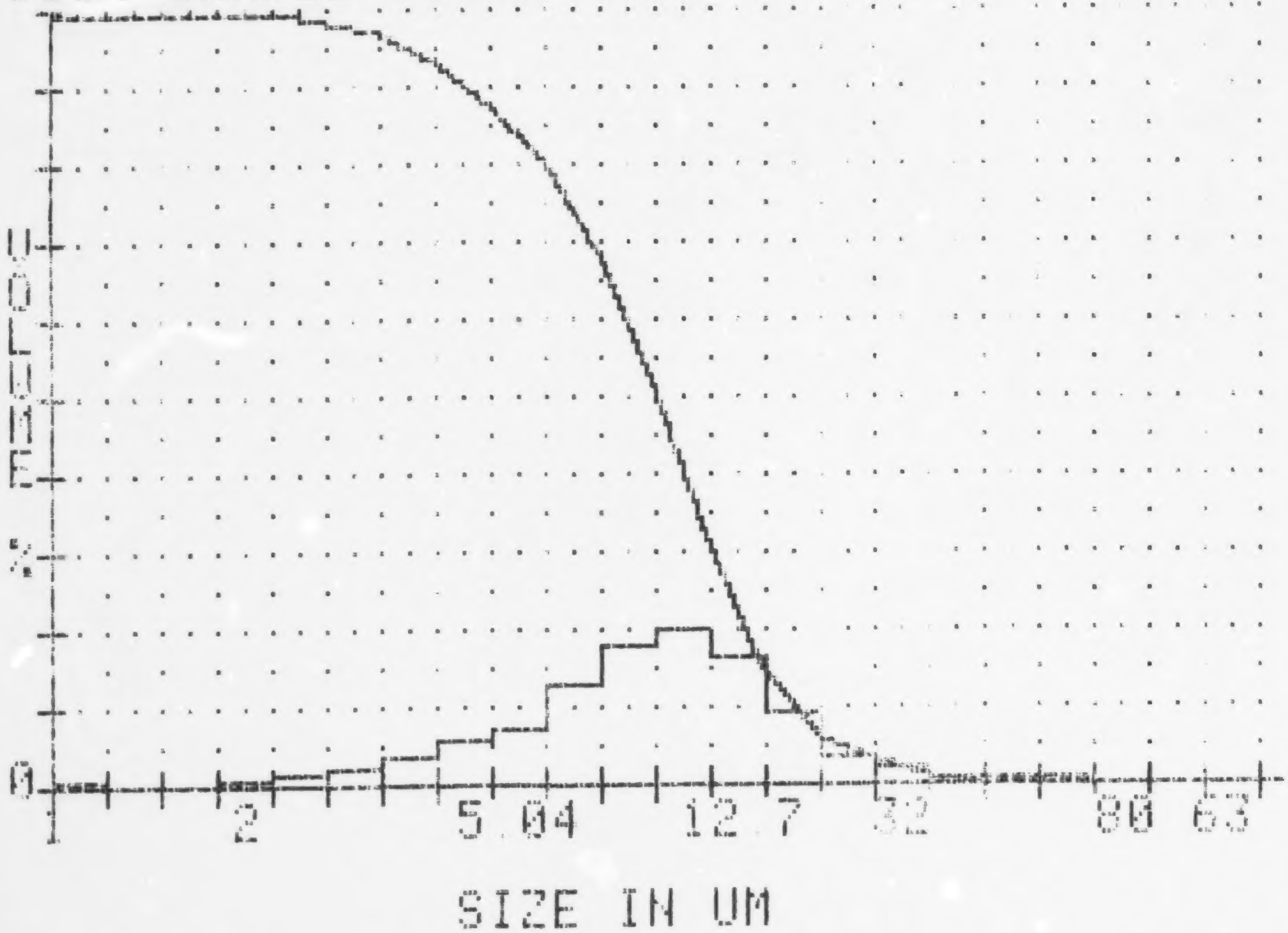
```
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

DATE: NOV 13 87
SAMPLE: J3242   SODA ASH LEACH TAILS
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#    SIZE            DIFF        CUM
                        VOL %       VOL %
****************************************
1       1               .22         100
2       1.26            0           99.78
3       1.59            0           99.78
4       2               .4          99.78
5       2.52            .95         99.38
6       3.17            2.01        98.43
7       4               3.58        96.42
8       5.04            5.56        92.83
9       6.35            7.17        87.27
10      8               12.45       80.11
11      10.08           17.27       67.65
12      12.7            19.92       50.39
13      16              16.27       30.47
14      20.16           8.85        14.2
15      25.4            2.96        5.35
16      32              1.7         2.39
17      40.32           .39         .69
18      50.8            .15         .31
19      64              .15         .15
20      80.63           0           0
21      101.59          0           0
22      128             0           0


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                   12 UM
MEDIAN:                 12.76 UM
MODE                    14 UM
STANDARD DEVIATION:     1.72 UM
COEF. VAR.:             14.36 %
SKEWNESS:               .92 NEGATIVE
KURTOSIS:               1.41 PLATYKURTIC
```

100% SAMPLE J3242 SODA ASH LEACH TAILS



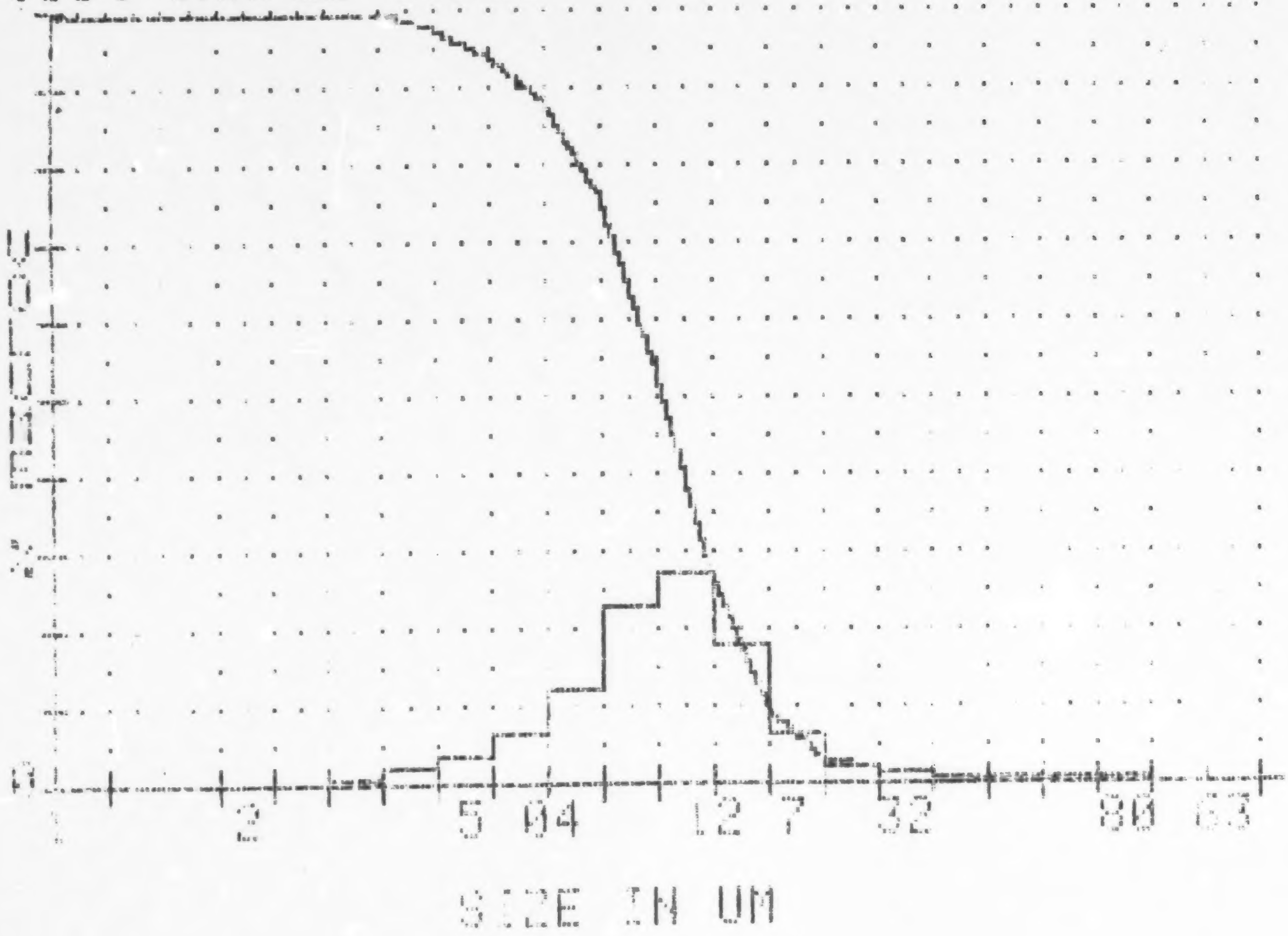
```
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

DATE: NOV 13 87
SAMPLE: J3243  CAUSTIC SODA LEACH TAILS
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#    SIZE            DIFF        CUM
                        VOL %       VOL %
****************************************
1       1               0           100
2       1.26            0           100
3       1.59            0           100
4       2               0           100
5       2.52            0           100
6       3.17            .71         100
7       4               2.07        99.29
8       5.04            3.54        97.23
9       6.35            5.9         93.68
10      8               11.93       87.78
11      10.08           22.56       75.85
12      12.7            27.18       53.29
13      16              17.48       26.11
14      20.16           6.08        8.64
15      25.4            1.49        2.56
16      32              .83         1.07
17      40.32           .08         .24
18      50.8            0           .16
19      64              0           .16
20      80.63           .16         .16
21      101.59          0           0
22      128             0           0


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                     12.59 UM
MEDIAN:                   13.06 UM
MODE                      13.68 UM
STANDARD DEVIATION:       1.5 UM
COEF. VAR.:               11.92 %
SKEWNESS:                 .98 NEGATIVE
KURTOSIS:                 1.12 PLATYKURTIC
```

100% SAMPLE J3243 CAUSTIC SODA LEACH TAILS



CAB

Fabrication of FCC Catalysts from Suncor Flyash Leach Residue for Carbovan Inc.

Progress Report #2

Carbovan Inc.
2200 Argentia Road
Mississauga, Ontario
L5N 2K7

Attn: Mr. Nairn McQueen

Submitted by:

V. I. Lakshmanan
C. A. Booth
G. M. Freeman
Mineral Resources

ORF Account No. 41-10874
DSS Contract Serial No. 23440-7-9124/01-SQ

December 16, 1987

ORF

Fabrication of FCC Catalysts from Suncor Flyash Leach Residue For Carbovan Inc.

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4. CHEMICAL ANALYSIS 4

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1. INTRODUCTION

In Progress Report No. 1, a summary report that included earlier ORF and S.R.C. test work on carbovan leach residue was submitted.

tails.

tails.

The present report includes the physical and chemical characterization of i) Suncor boiler hopper ash (BHA), identified as J3239 ii) Electrostatic Precipitator Ash (ESP), identified as J3240, iii) carbon flotation tails obtained from typical carbovan process feed (3 ESP: 1 BHA), identified as J3241, iv) Leach tail obtained after caustic leach, identified as J3242, and v) leach tail obtained after caustic/soda ash leach, identified as J3243. The results are discussed.

tails.

2. XRD, SEM, EDX RESULTS

The bulk samples for SEM with EDX were mounted on brass stubs and coated with Au. SEM was carried out with a ISI DS-130 research instrument with an accelerating voltage of 30 KV. The bulk samples were examined by x-ray powder diffraction using a RIGAKU.

2.1 Results

Table 1 (see Appendix I) shows the mineralogy of five samples which contained a large amount of amorphous material in BHA, float-tails, and ESP samples, whereas NaOH-leach and soda ash leach samples contained mainly zeolite. Zeolite can be classified as analcime, wairakite, and wellsite. Between analcime and wairakite their d-spacings are slightly different showing at bottom of Table 1. Monohydrocalcite ($CaCO_3 \cdot H_2O$) was also found in Float-tails sample. Trace of calcite was determined by SEM in soda-ash-leach sample (see Table 6 in Appendix I).

The XRD original patterns are attached for checking. High background suggests the content of amorphous materials (or organic materials).

SEM examinations of the samples showed the following characteristic morphology and their chemistry. In the BHA sample, we found many barite grains showing S and Ba signals. Spherical materials are common in this sample showing Al, Si, S, K, Ca, Ti, V, Ni peaks with high Fe peak. Three elements of Ti, V, and Ba have similar energy (KeV) as shown in bottom of Table 2 (see Appendix I). Attached are two SEM pictures with EDX (in Appendix I).

?

In the Float-tails sample spherical materials are also common as BHA sample. Si content is a little bit higher than BHA's. Size of spherical materials are various as shown in SEM picture. K-feldspar grain was found which agreed with XRD data (Table 3 in Appendix I).

ESP

In the EPS sample spherical materials show similar chemistry as BHA and Float-tails samples, but their surfaces are rough correlating higher V content. A quartz grain was found showing spherical materials on the surface (Table 4 in Appendix I).

In the NaOH-leach sample, many zeolite crystals which showed orthorhombic or pseudo-cubic (see SEM pictures) were observed. The most of zeolite can be classified as analcime, wairakite, or wellsite showing Na, Al, Si, K, Ca, Ti, V, Fe and Ni signals. There are also small lath crystals of clinoptilolite in the sample (see centre of SEM picture 7) indicating similar composition (Table 5*8 in Appendix I). The iron content was relatively low compared with un-leached samples. The sample showed a trace of V (Table 5 in Appendix I).

Soda ash leach sample showed well-developed zeolite. Cubo-octahedral crystals of analcime are common showing Na, Al, Si, K, Ca, Ti, V, Fe and Ni signals. A small amount of clinoptilolite crystals (lath-like) are also visible in this sample containing Mg. Both V and Fe contents are lower than any other samples. Few calcite grains were observed showing strong Ca signal (Table 6 in Appendix I).

We have observed several grains for each sample of the samples, and showed only one or two of them here which are a typical view.

XRD data for the bulk sample do not show any clay minerals. If we need clay mineralogy of it, we have to correct <2 um size fraction for XRD and TEM works. If we need organic material information (or amorphous materials), we have to do SIMS, Auger, ESCA, TEM with E.D. examinations.

Detailed results are shown in Appendix I.

References

Glauco Gottardi and Ermanno Galli (1985) Natural zeolites. Springer-Verlag Berlin Heidelberg New York Tokyo.

Mumpton, F. A. (1977) Mineralogy and geology of natural zeolites. Miner. Soci. of America, Vol. 4.

Welton, J. E. (1984) SEM petrology atlas. Amer. Assoc. of Petroleum Geologists.

Sudo T. (1987) Zeolite-clay mineral relations in sedimentary rocks from Niigata and Hokkaido oil fields - clue to recognition of their diagenetic reactions. Report of O.R.D. of Japan, 1-22.

3. SURFACE AREA AND PARTICLE SIZE ANALYSIS

Surface area measurements were made using micromeritics ORR SAPV (BET Analyser) Model 2100. The samples were outgassed at room temperature for 24 hours to remove any residual adsorbed species. Particle size measurements were made using the Coulter Counter. The results show the surface area for BHA, ESP, 3 ESP:1 BHA, caustic leach, caustic/soda ash leach, as 5.1, 3.0, 1.9, 42.3 and 24.0 on 218.

Particle size analysis show mean particle diameter for i) BHA, ii) ESP, iii) 3 ESP: 1 BHA, iv) caustic leach, and v) caustic/soda ash leach as 16.07 um, 11.19 um, 9.77 um, 12.00 um and 12.59 um respectively.

Detailed results are shown in Appendix II.

4. CHEMICAL ANALYSIS

The chosen five samples BHA, ESP, decarbonized flotation tails, caustic leach tails and caustic-soda ash leach tails were chemically analyzed for SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O, Fe_2O_3, MnO, TiO_2, P_2O_5, and Loss on Ignition (LOI). Trace analyses were performed for Cr, Rb, Sr, Y, Zr, Nb, and Ba.

The results are shown in Appendix III.

5. FUTURE WORK

During the next month specification analysis for currently available zeolite products by literature search and from industrial sources will be obtained. Catalytic properties of unmodified leach residue and leach feed also will be studied. The samples discussed in this report will be analyzed for pore size distribution using the mercury porosometer method.

Craig A Booth
C. A. Booth
Project Scientist
Mineral Resources

Gm. Freeman
G. M. Freeman
Operations Manager
Mineral Resources

V. I. Lakshmanan
Project Manager
Mineral Resources

APPENDIX I: XRD, SEM, EDX Results

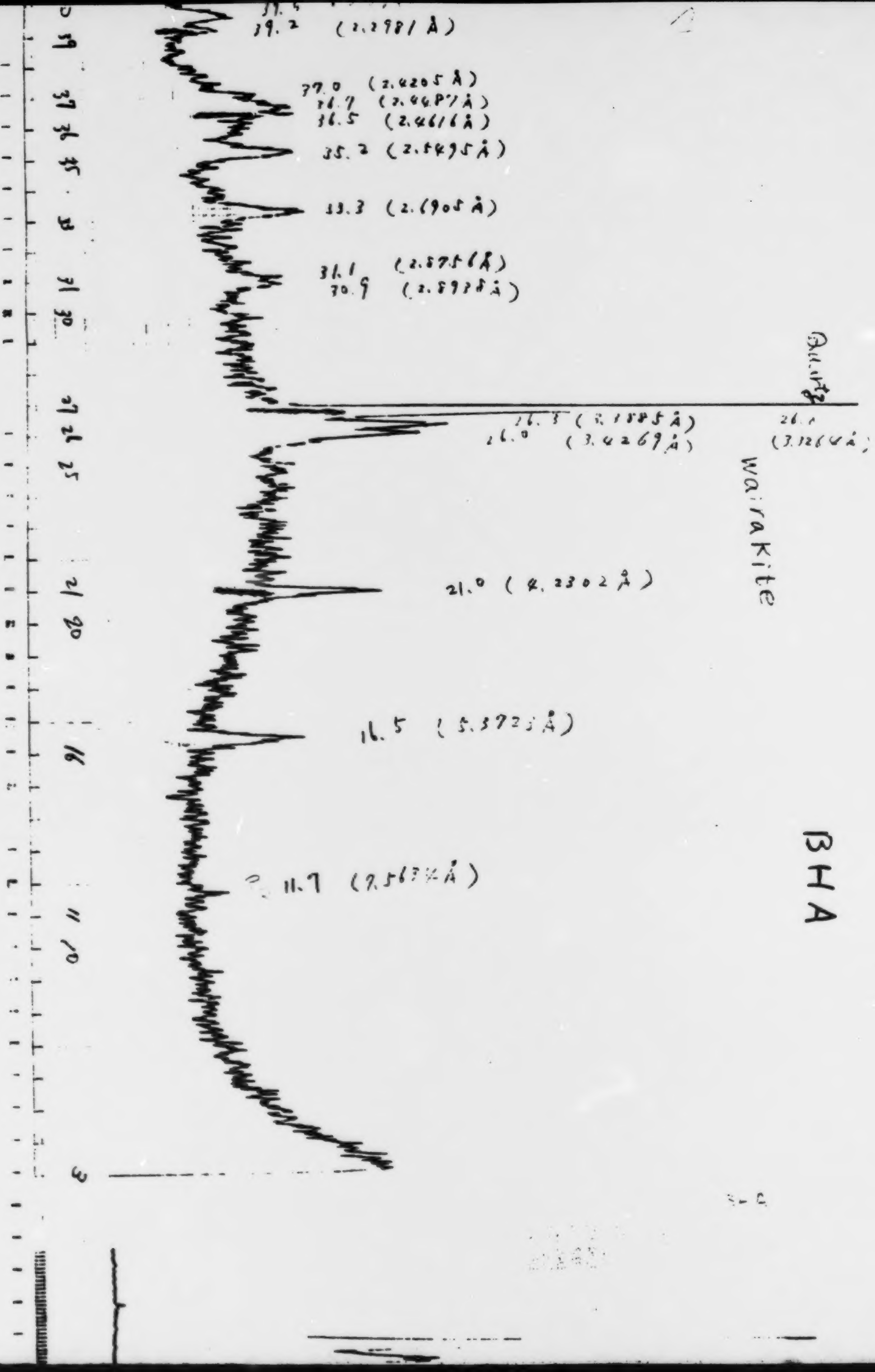
Table 1 : XRD data

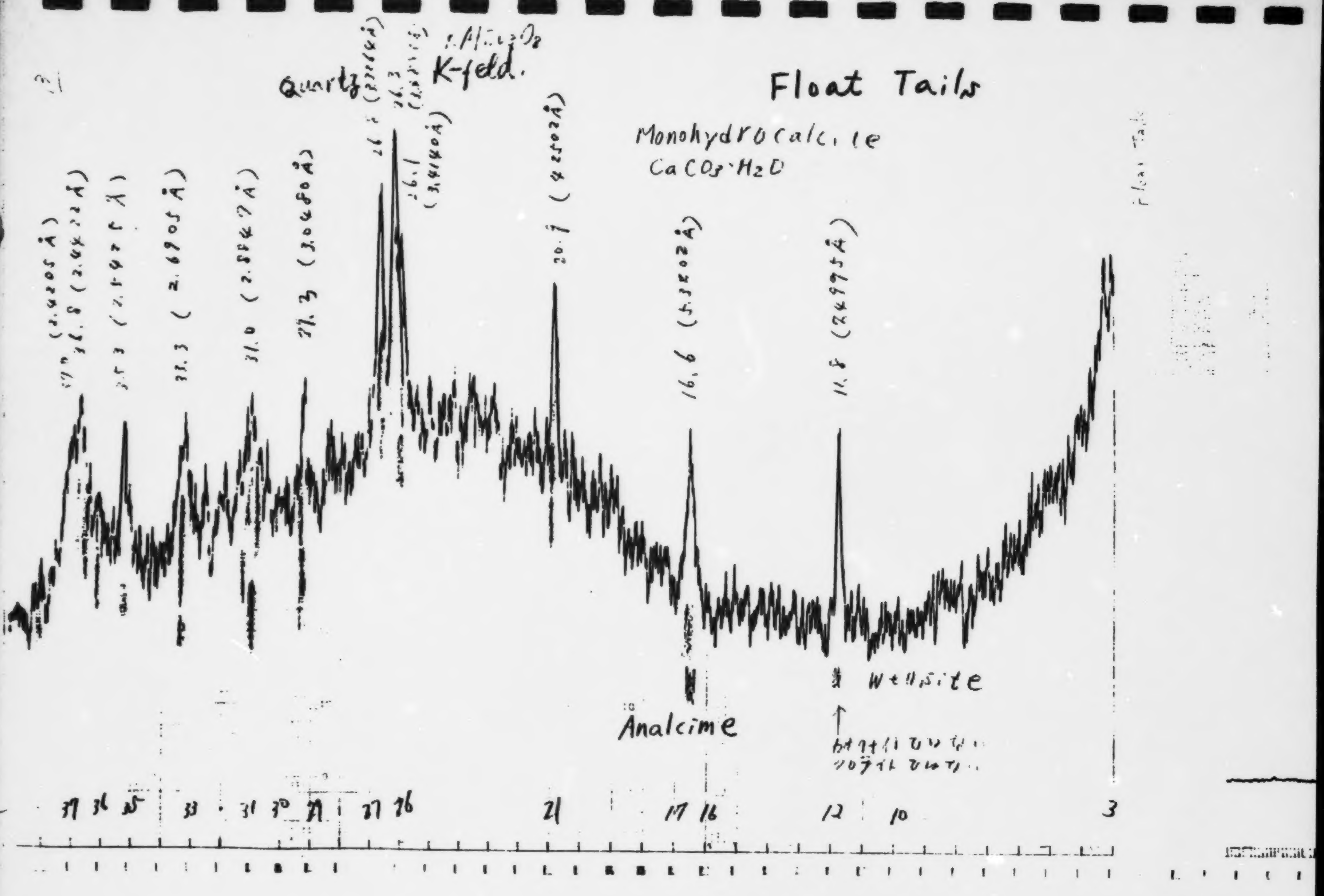
Sample \ mineral	Amorphous	Quartz	K-feld.	Analcime	Wairakite	Wellsite	Monohydrocalcite
BHA	+++	+++			++		
Float Tails	++++	++	++	+		++	++
ESP	++++				++		
NaOH Leach	+			+++	++	++	
Soda ash Leach				++++			
		SiO_2	$KAlSi_3O_8$	$Na_{17}Al_{17}Si_{31}O_{96}\cdot 16H_2O$ ~ $Na_{14}Al_{14}Si_{34}O_{96}\cdot 16H_2O$		$(Ba,Ca,K_2)Al_2Si_3O_{10}\cdot 3H_2O$	$CaCO_3\cdot H_2O$

Analcime	Wairakite
	6.85 Å
5.57 Å	5.57
4.83	4.84
	3.64
3.42	3.42 3.39
2.916	2.909 2.897
.683	2.680 2.67

8.1 Å
7.2
6.4
5.0
4.07
3.153 (100 B)
2.903
2.688 (80 B)
2.501
2.342
2.217

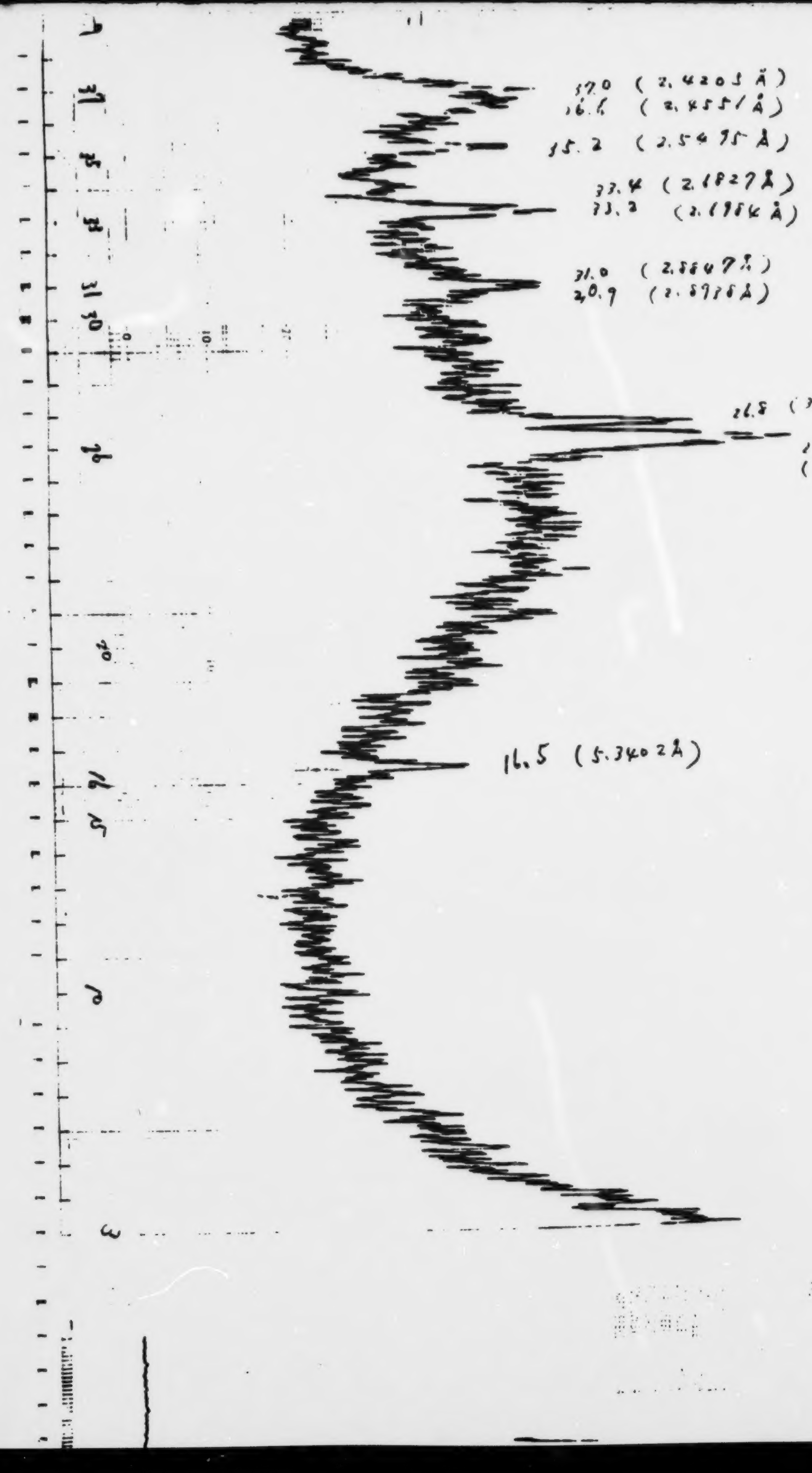
5.271 Å
4.327 (100)
3.072 (77)
3.042 (14)
2.825 (45)


39.2 (2.2981 Å)
37.0 (2.4205 Å)
36.7 (2.4487 Å)
36.5 (2.4616 Å)
35.2 (2.5495 Å)
33.3 (2.6905 Å)
31.1 (2.8756 Å)
30.9 (2.8938 Å)
Quartz
26.5 (3.1885 Å)
26.0 (3.4269 Å)
26.1 (3.1264 Å)
wairakite
21.0 (4.2302 Å)
16.5 (5.3723 Å)
11.7 (7.5634 Å)
BHA
39
37
36
35
33
31
30
27
26
25
21
20
16
11
10
3

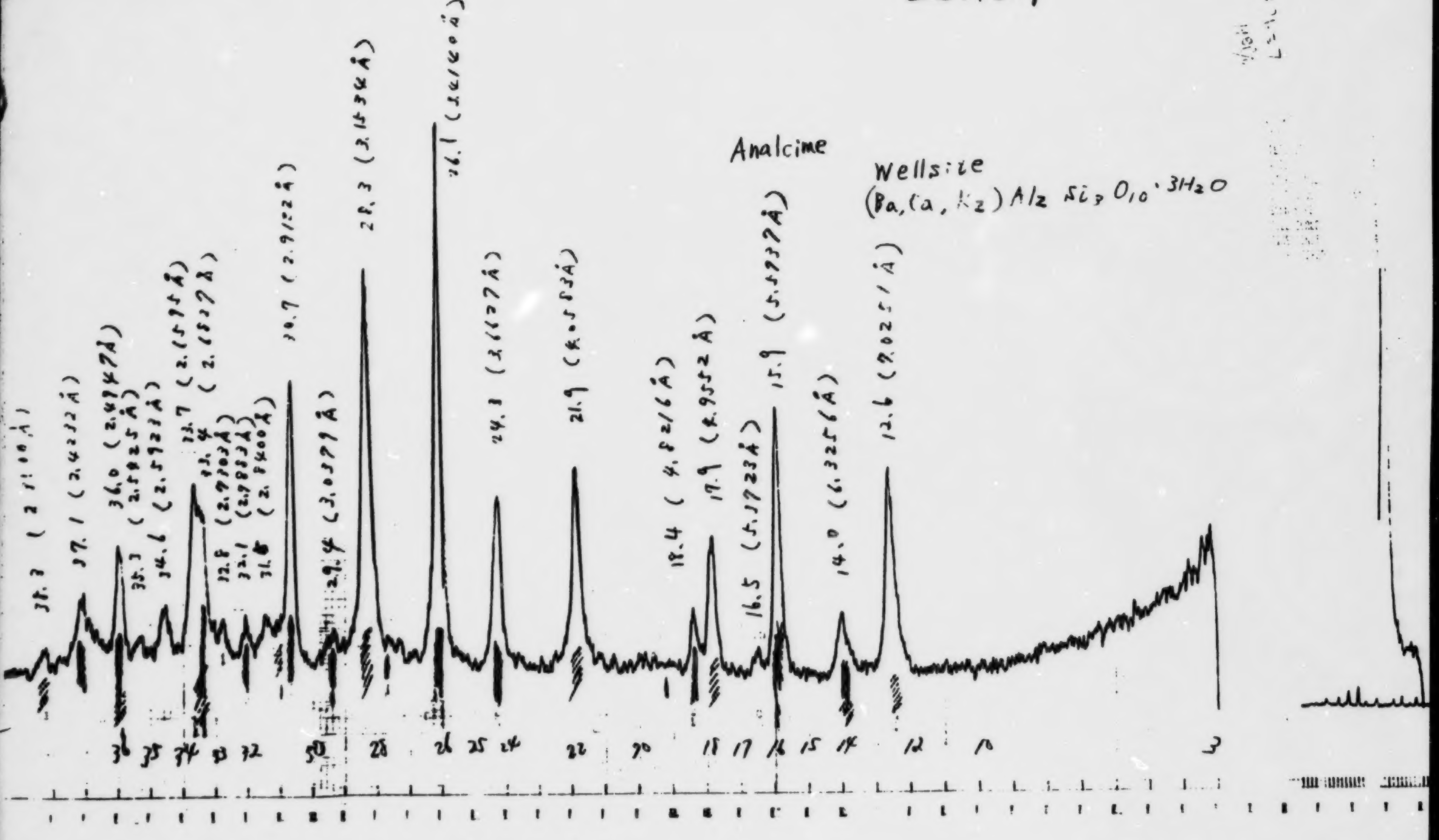

Float Tails
Monohydrocalcite
CaCO3·H2O
Quartz
K-feld.
KAlSi3O8
37.0 (2.4205 Å)
36.8 (2.4422 Å)
35.3 (2.5407 Å)
33.3 (2.6905 Å)
31.0 (2.8847 Å)
29.3 (3.0480 Å)
26.6 (3.3484 Å)
26.3 (3.3860 Å)
26.1 (3.4140 Å)
20.9 (4.2502 Å)
16.6 (5.3302 Å)
11.8 (7.4995 Å)
Analcime
Wellsite
Float Tails
37
36
35
33
31
30
29
27
26
21
17
16
12
10
3

ESP

rakite


37.0 (2.4203 Å)
36.6 (2.4551 Å)
35.2 (2.5495 Å)
33.4 (2.6827 Å)
33.2 (2.6984 Å)
31.0 (2.8847 Å)
30.9 (2.8938 Å)
26.8 (3.3264 Å)
26.2 (3.4012 Å)
16.5 (5.3402 Å)
3
16
20
26
30
31
33
35
37

NaOH
LEACH


Analcime
Wellsite
$(Ba, Ca, K_2)Al_2Si_3O_{10} \cdot 3H_2O$
38.3 (2.3500 Å)
37.1 (2.4232 Å)
36.0 (2.4947 Å)
35.3 (2.5425 Å)
34.6 (2.5923 Å)
33.7 (2.6595 Å)
33.4 (2.6827 Å)
32.8 (2.7303 Å)
32.1 (2.7883 Å)
31.8 (2.8400 Å)
30.7 (2.9122 Å)
29.4 (3.0379 Å)
28.3 (3.1534 Å)
26.1 (3.4160 Å)
24.3 (3.6627 Å)
21.9 (4.0553 Å)
18.4 (4.8216 Å)
17.9 (4.9552 Å)
16.5 (5.3723 Å)
15.9 (5.5737 Å)
14.0 (6.3256 Å)
12.6 (7.0251 Å)
36
35
34
33
32
30
28
26
25
24
22
20
18
17
16
15
14
12
10
3

SODA ASH
LEACH

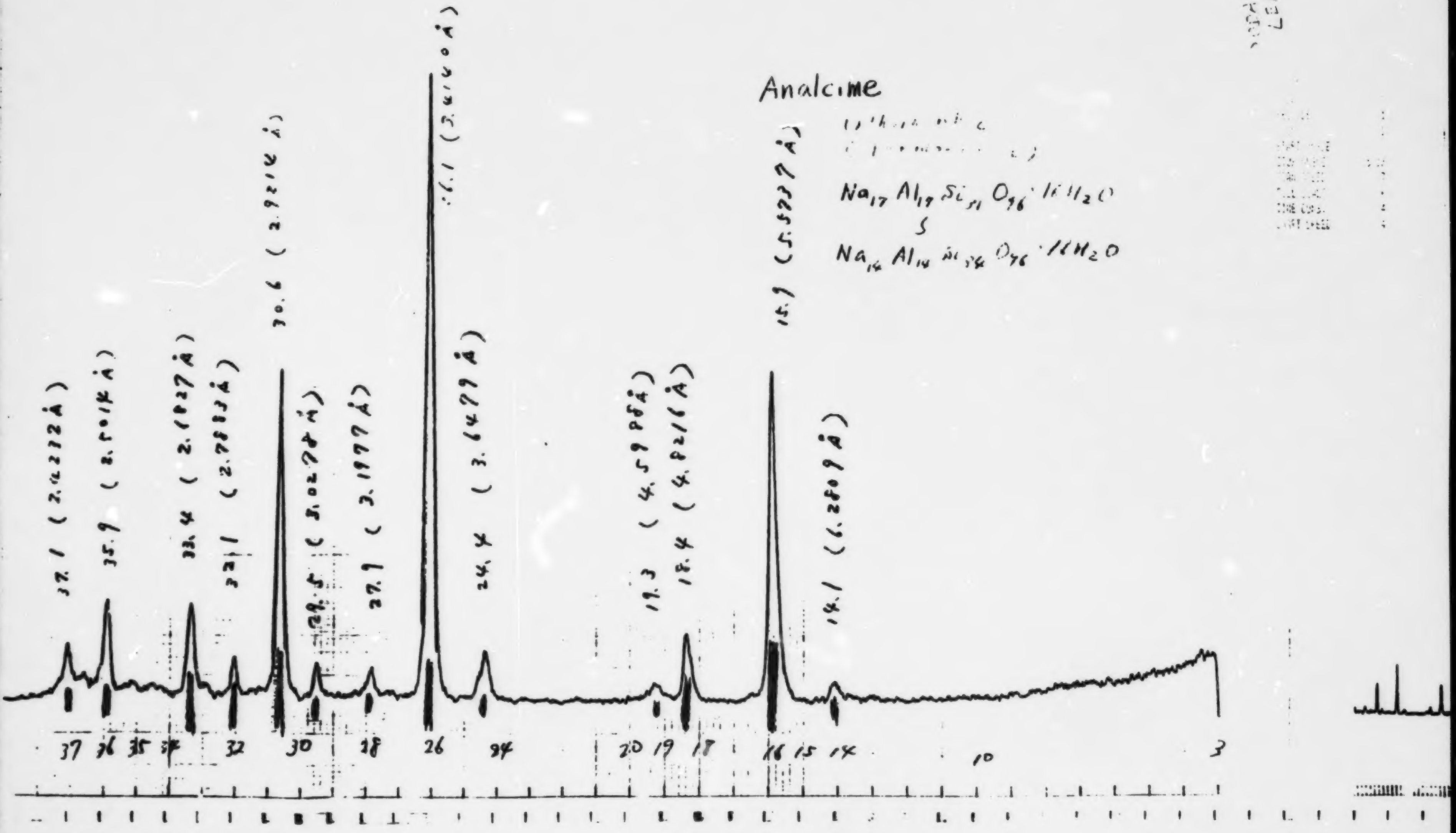
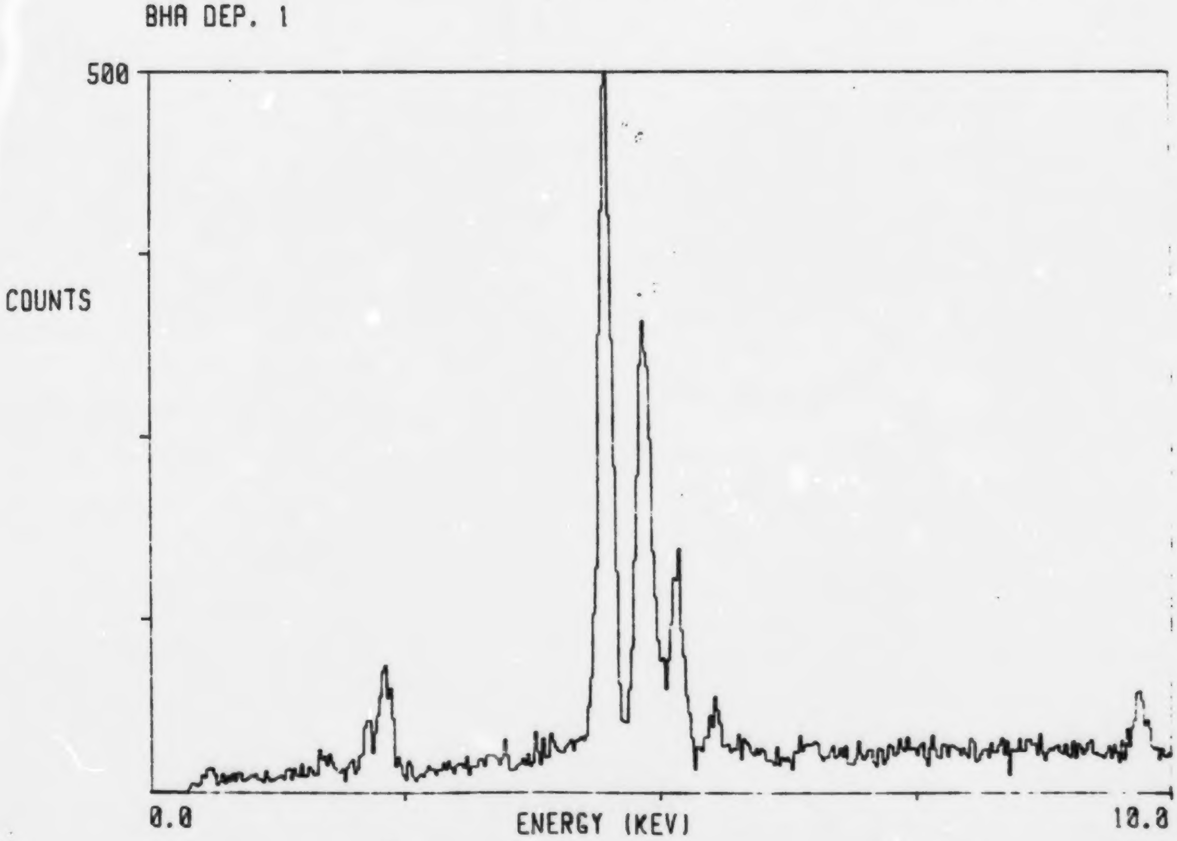


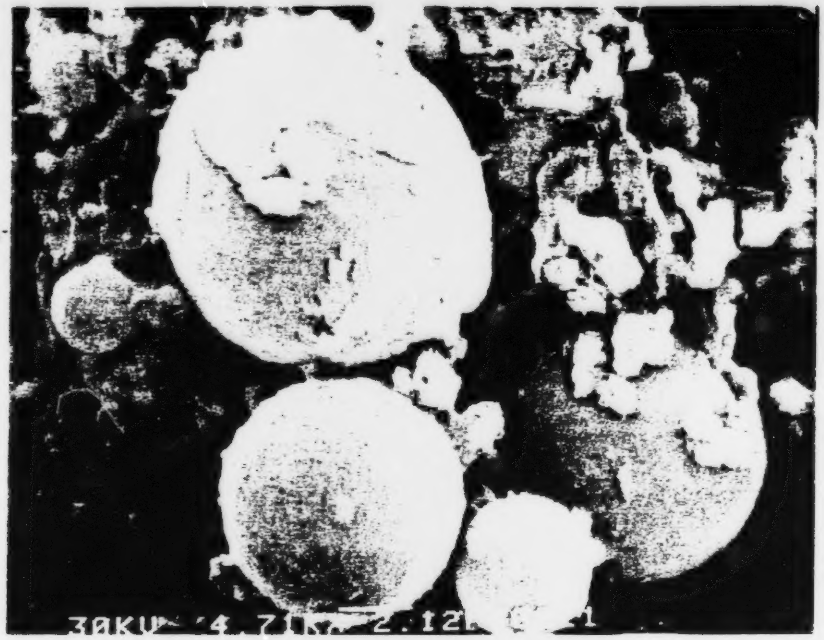
Table 2 : SEM with EDX data (BHA)

Sample	attached SEM	Na	Mg	Al	Si	S	K	Ca	Ti	V	Ba	Fe	Ni
BHA	(1) Barite					+					++++		
	2. K-feld.			+	+++		+++						
	3. Barite			tr.	tr.	++					+++		
	4. Barite				+	++					++++	++	
	5.			+	++	+		tr.	+	++		++++	tr.
	6.			+	++	tr.	+	+	+	+		++++	tr.

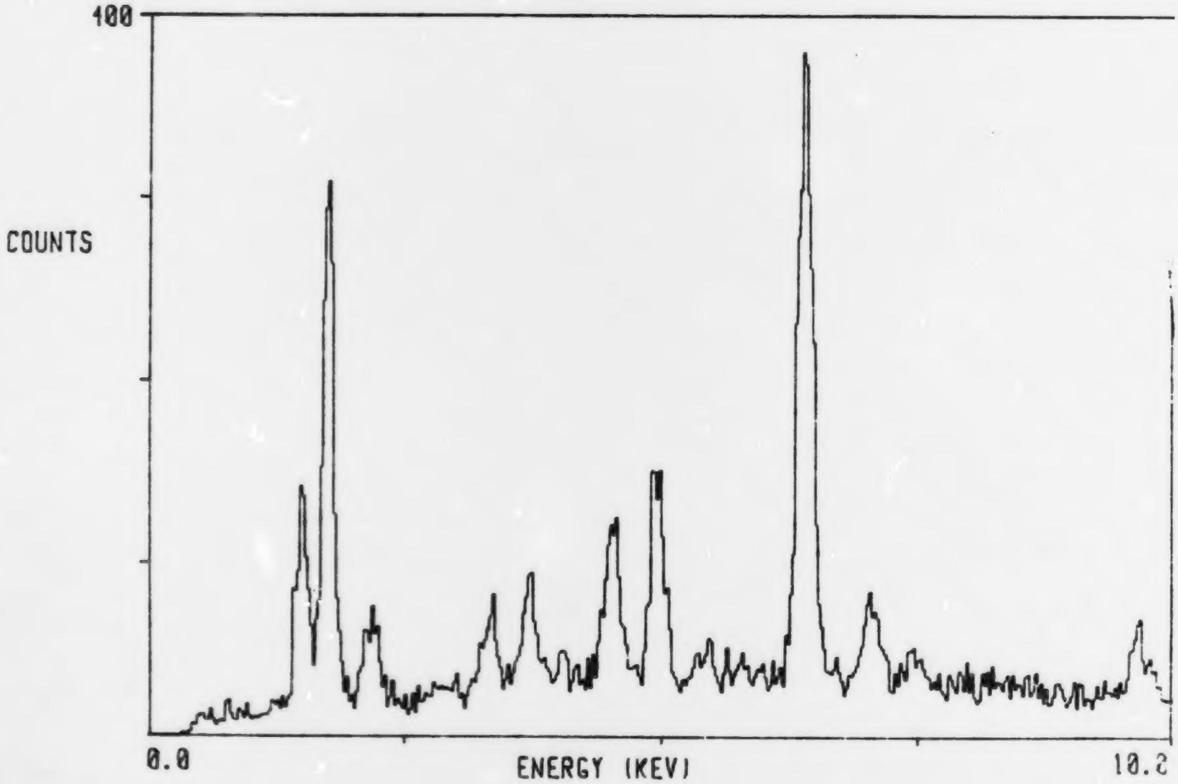
Ti	Kα 4.510	Kβ 4.931		
V		Kα 4.952	Kβ 5.427	
Ba	Lα 4.467	Lβ 4.828	Lγ1 5.531	LII 5.623

4.22µ 001


BHA DEP. 1
500
COUNTS
0.0
ENERGY (KEV)
10.0

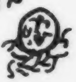
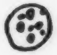
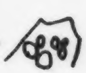
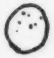
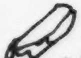
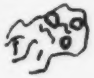

30KV 4.71K 2.12

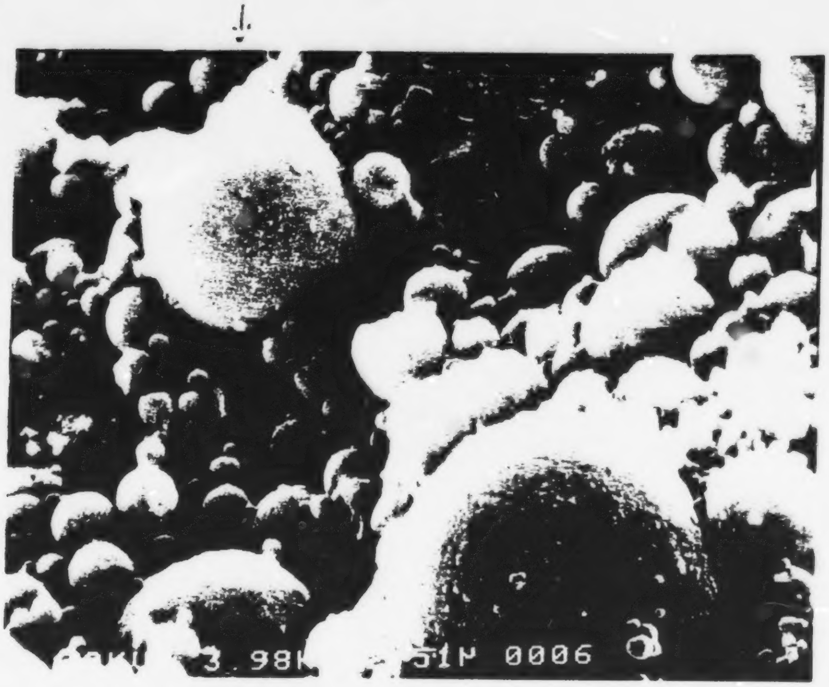
BHA DEP. 6



Al Fe [illegible]

Table 3: SEM with EDX data (Float Tails)

Sample	Na	Mg	Al	Si	S	K	Ca	Ti	V	Ba	Fe	Ni
Float Tails												
1. 			+	+				+			++++	
2. 									tr.		++++	
3. 			+	++	++	tr.	tr.	tr.	+		+	
SEM 4. 			++	+++		+	+	+	+		++	+
5.  K-feld.			+	+++	tr.	++						
6. 			+	+++	tr.		tr.	+	+		++++	+


3.98K
51M 0006

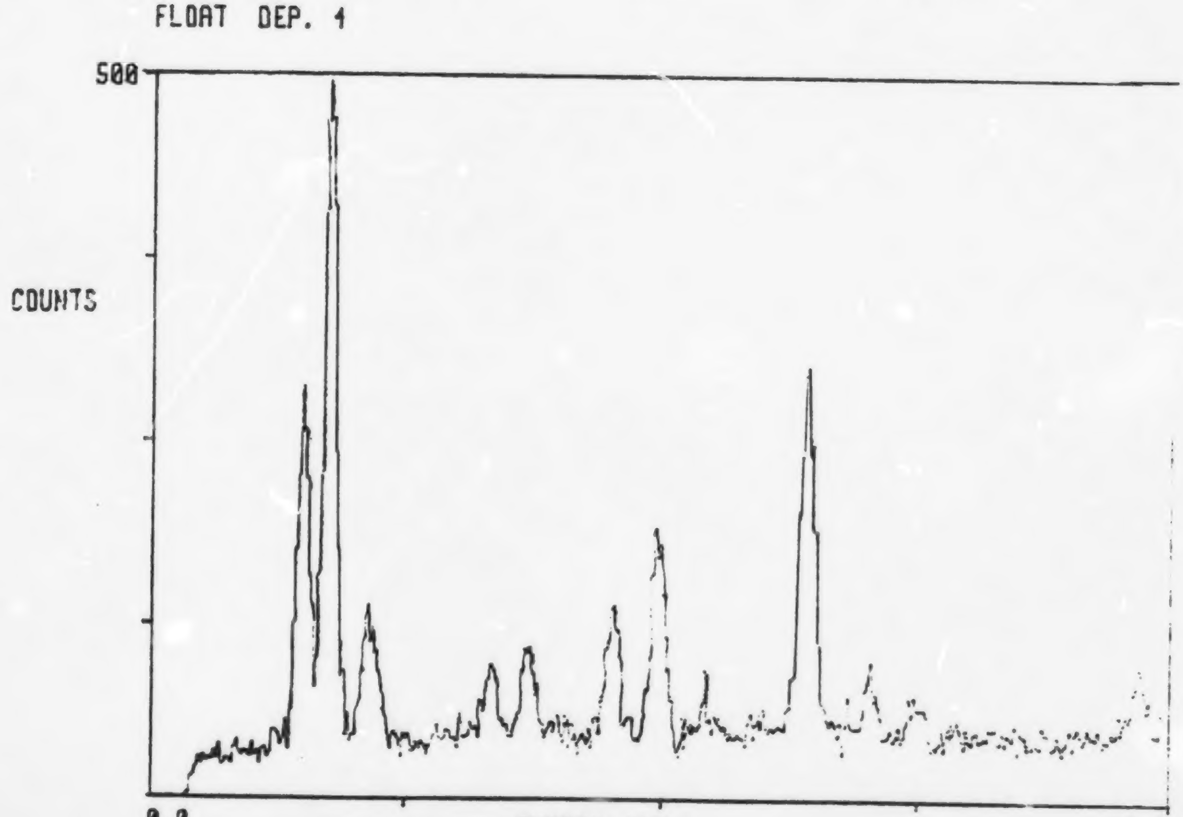
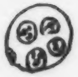
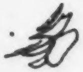
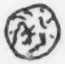
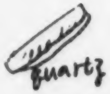
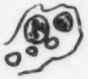
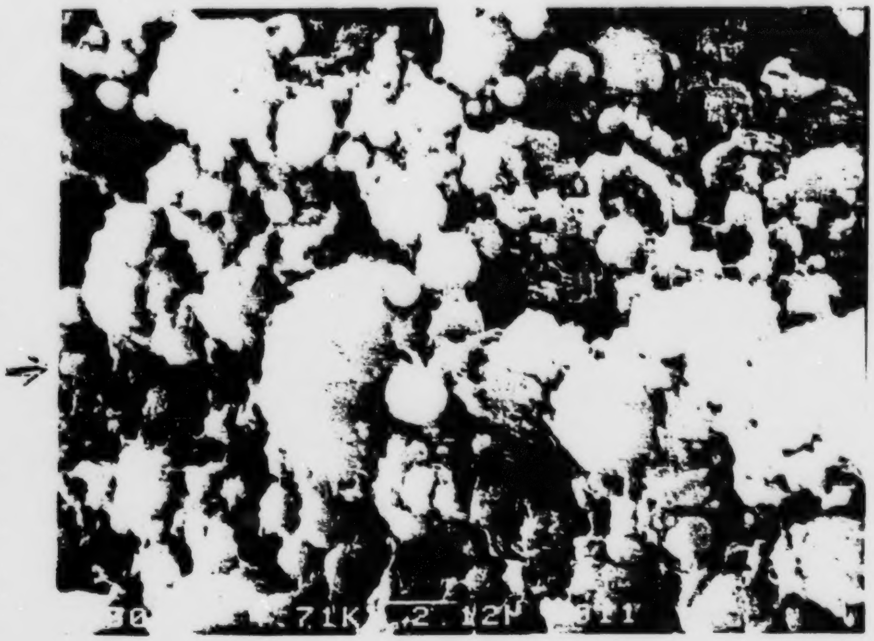

FLOAT DEP. 4
500
COUNTS
0.0
ENERGY (KEV)
10.0
Al Si
K

Table 4: SEM with EDX data (EPS)

Sample	Na	Mg	Al	Si	S	K	Ca	Ti	V	Ba	Fe	Ni
ESP												
1. 			+	++	tr.	+	+	++	++		+++	+
2. 			+	+++	tr.	+	tr.	tr.	tr.		+	
SEM 3. 			+	++	+	+	+	+	++		+++	+
4. 			+	+++	tr.				tr.		+	tr.
5. 			++	++	tr.	+	+	+	++		+++	+


30 .71K 2 12P 011

ESP DEP. 3

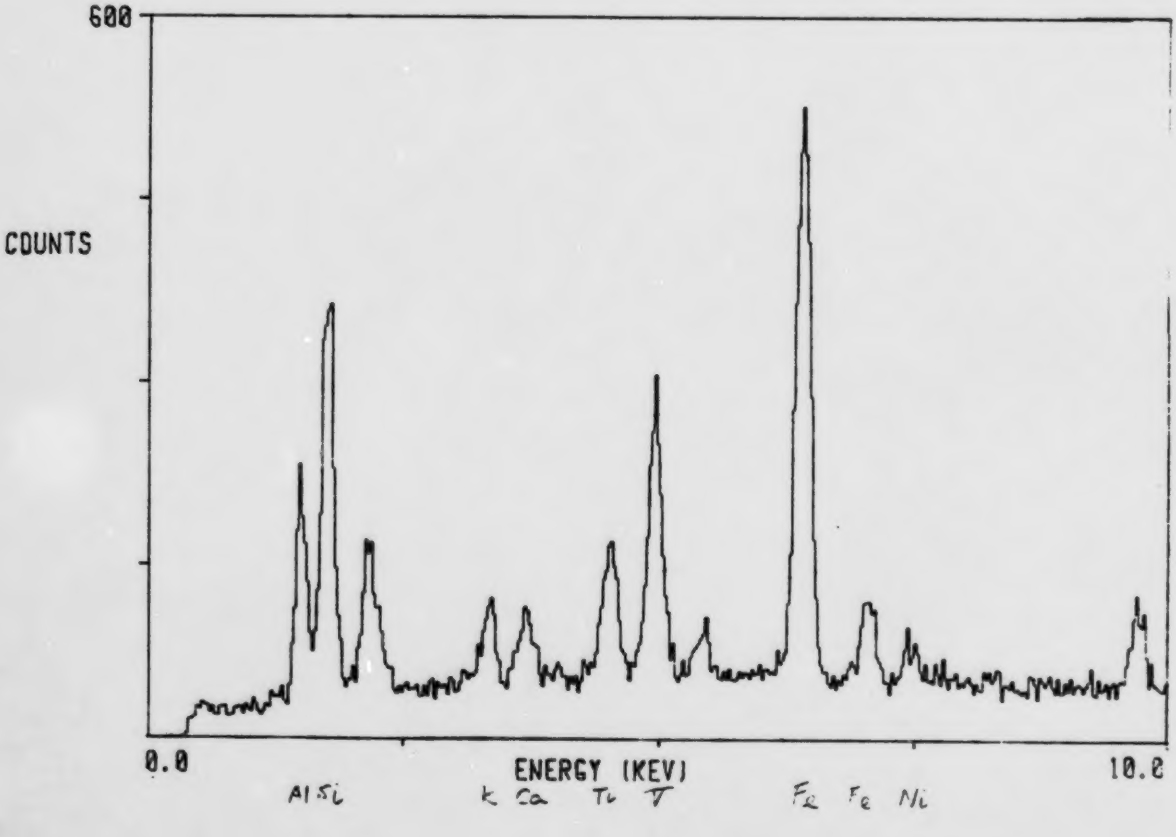
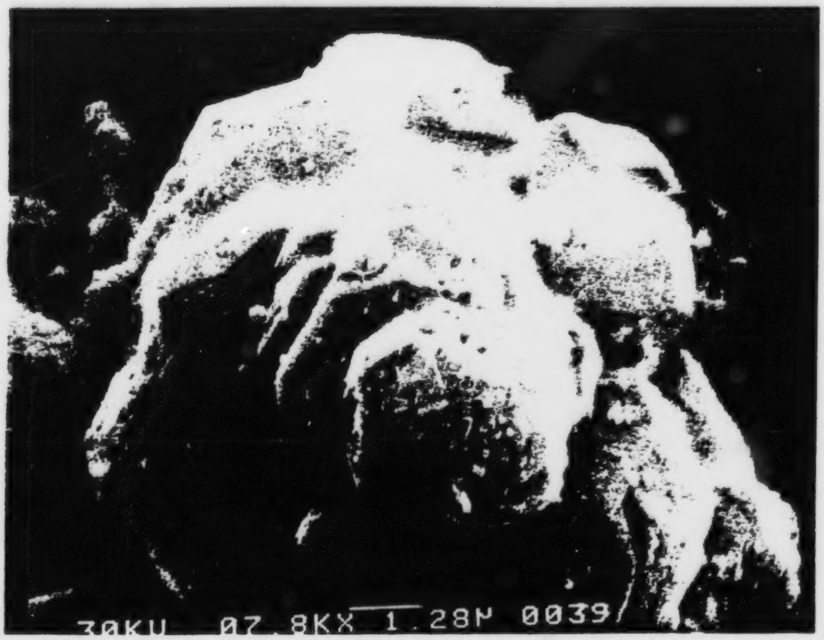

600
COUNTS
0.0
ENERGY (KEV)
10.0
Al Si
K Ca
Ti
V
Fe
Fe
Ni

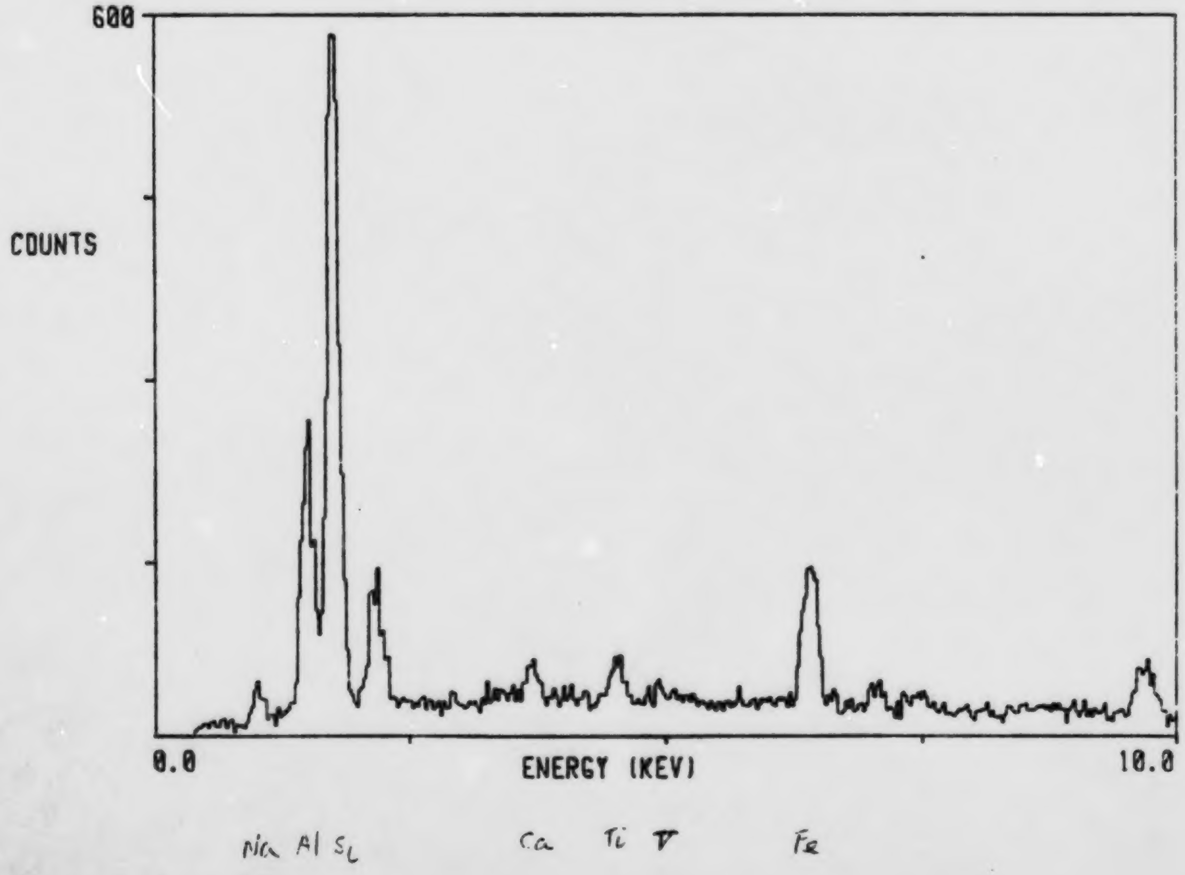
Table 5 : SEM with EDX data (NaOH leach)

Sample NaOH leach	Na	Mg	Al	Si	S	K	Ca	Ti	V	Ba	Fe	Ni
1.	tr.		+++	+++		tr.	+	+	tr.		+++	+
2.	tr.		++	+++		+	+	+			+	
3.	tr.		++	+++		+	+	+			++	
4.	tr.		++	+++		tr.	tr.	++	tr.		++	
SEM 5.	tr.		++	+++			tr.	tr.	tr.		+	
6.	tr.		++	+++	tr.	+	+	+	tr.		++	
SEM 7.	tr.		++	+++		tr.	tr.	tr.			+	
* 8.	tr.		++	+++		+	+	+	tr.		++	tr.
9.			+	++		+	+	+			++	

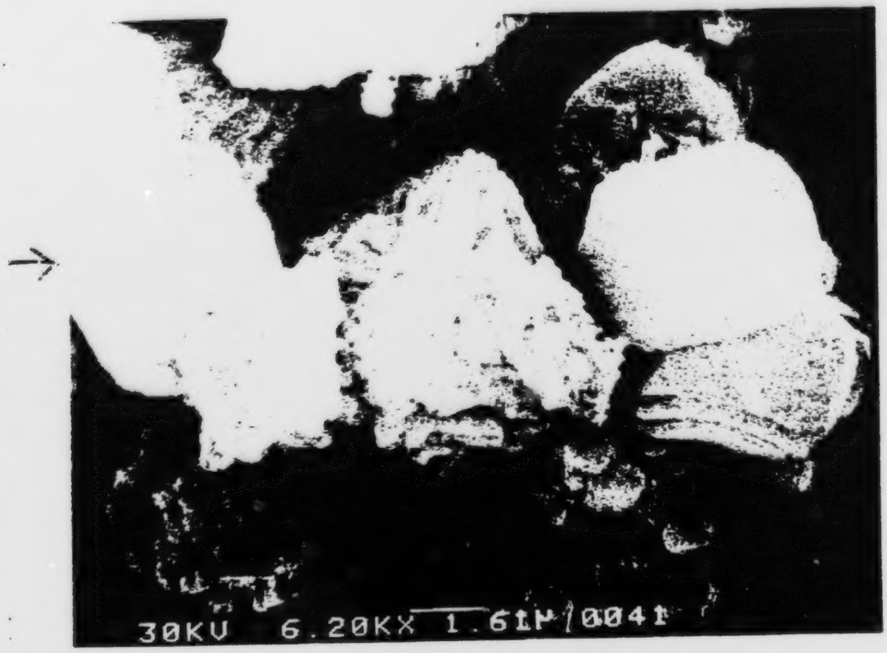
* clinoptilolite

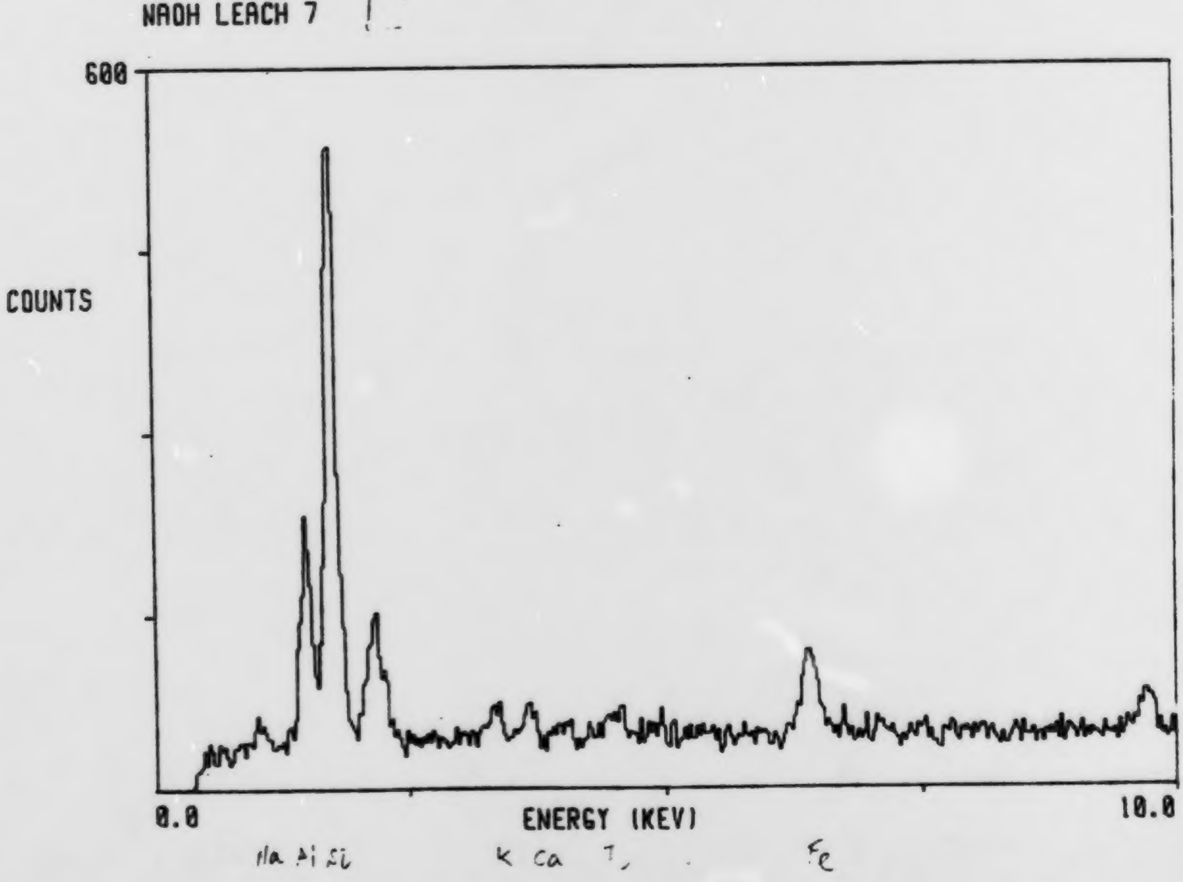
The most of grains are analcime, wairakite, or wellsite.


30KV 07.8KX 1.28μ 0039


NAOH LEACH 5

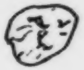
600
COUNTS
0.0
ENERGY (KEV)
10.0
Na Al Si
Ca
Ti V
Fe

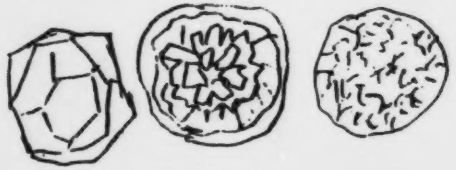

→
30KV 6.20KX 1.61µ 0041



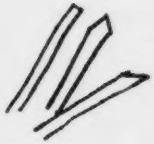
The EDX is for cubic crystal (arrow).

Table 6 : SEM with EDX data (Soda ash leach)

Sample	Na	Mg	Al	Si	S	K	Ca	Ti	V	Ba	Fe	Ni
Soda ash leach												
1. 			+	+		tr.	+	+			+++	+
SEM 2.	tr.		++	+++				tr.			+	
* 3.	tr.	tr.	++	++			+	++	tr.		+++	tr.
4. calcite			tr.	tr.			++++				tr.	
5.	tr.		+	+++		tr.	tr.	tr.	tr.		+	tr.
6.	+		++	+++			tr.				+	
7.			+	+++		tr.	tr.	tr.			+	

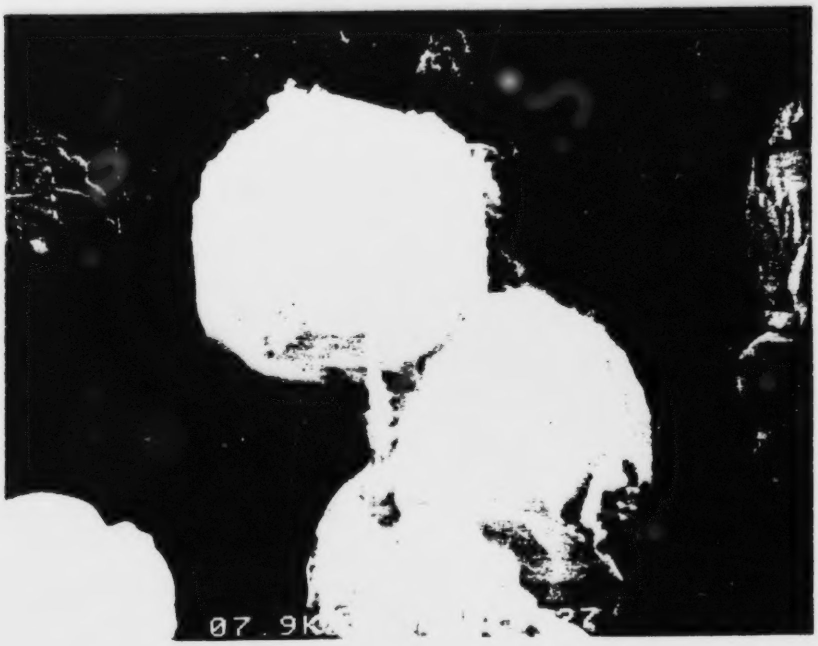


These are analcime.

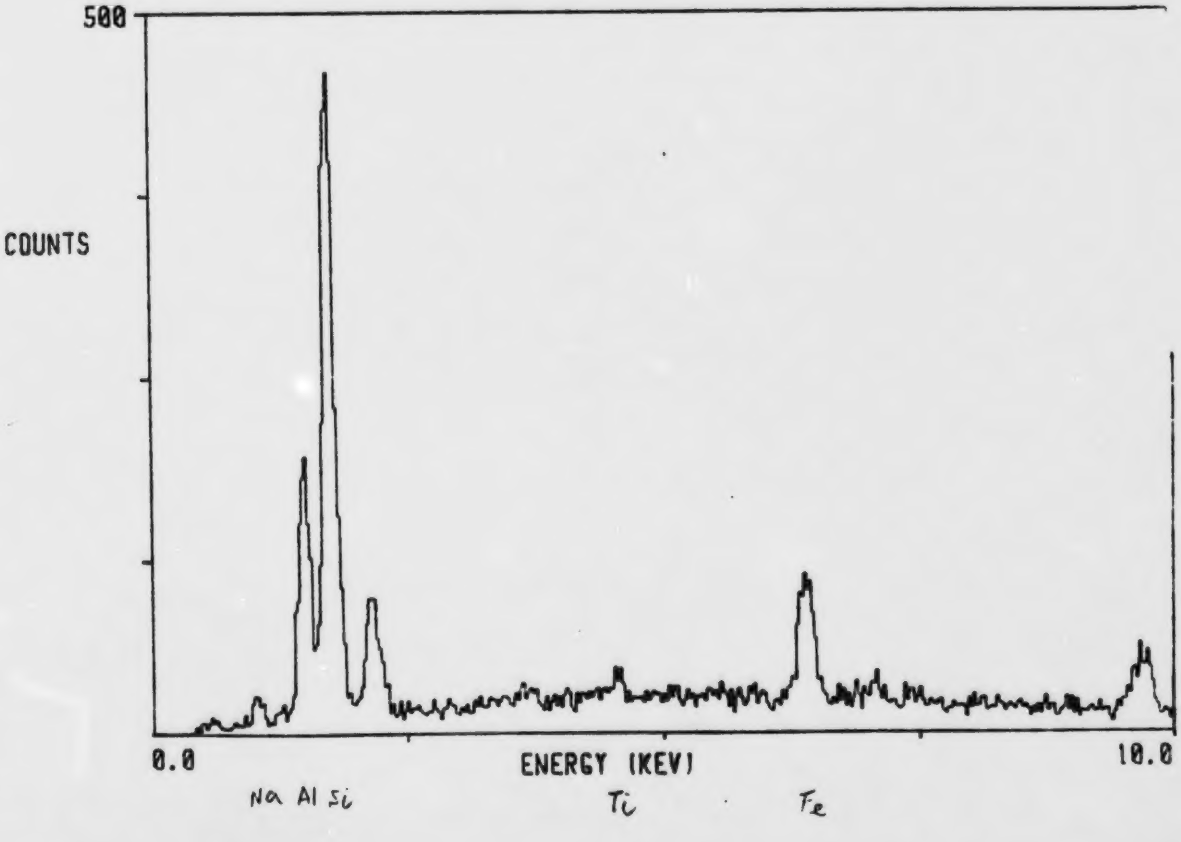
* 

clinoptilolite

$Na_6(Al_6Si_{30}O_{72})\cdot 24H_2O$



SODA ASH LEACH 2



APPENDIX II: Surface Area and Particle Size Analyses

C. Booth
PPCTR

December 3, 1987

REPORT NUMBER FPL 50005-87-91
IDENTIFICATION W.O. #27827

SPECIFICATIONS OF ORDER Surface Area and Particle Size Analyses on Five Samples

---

INTRODUCTION

Five Samples labelled J3239, J3240, J3241, J3242, J3243 were received for Surface Area and Particle Size Analyses.

Method

The samples were analyzed for Surface Area using the Micromeritics Orr SAPV Model 2100. The samples were outgassed at room terperature for 24 hours to remove any residual adsorbed species. The analyses were carried out using nitrogen as the adsorbate.

A representative portion of the sample was suspended in approximately 20 mL of Isoton II (a particle-free 0.8% Nacl aqueous electrolyte). The sample was then subjected to a low-power ultrasonic bath for thirty seconds to aid in de-agglomerating any loosely bound aggregates. A portion of the sample was then extracted by pipette for analysis on the Coulter Counter which is based on the electrical zone sensing method.

Results

The numerical, statistical and graphical data of the particle size analyses are attached. The surface area analyses are shown in Table 1.

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Project Technician

P. C. Markiewicz, M.Sc., M.A.Sc.
Project Scientist

K. L. Yan, Ph.D.
Section Manager

Report No. FPL 50005-87-91

Surface area reported

TABLE 1

SURFACE AREA ON FIVE SAMPLES

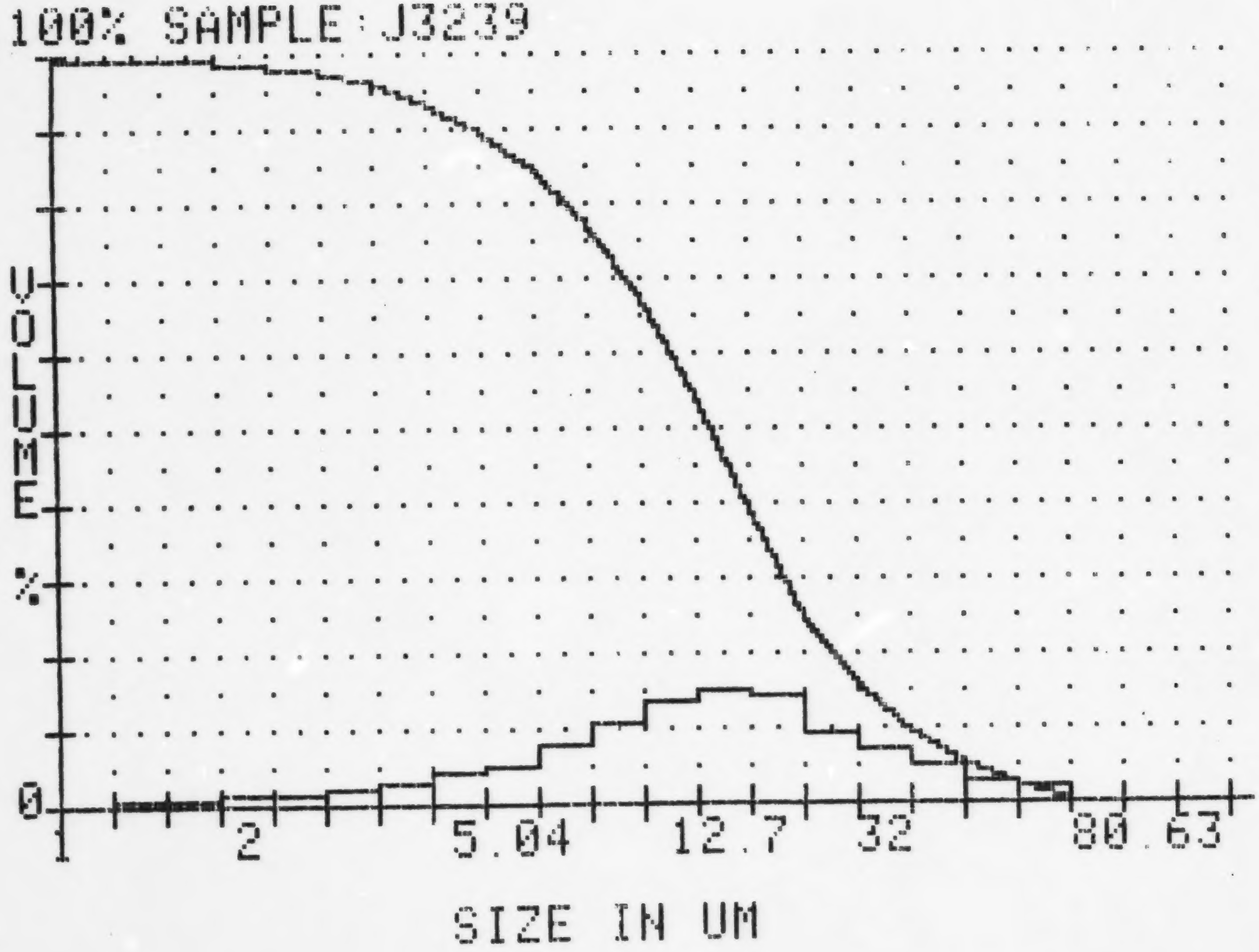
Sample I.D.	Surface Area (m^2/g)	
J3239	5.1	
J3240	3.0	
J3241	1.9	
J3242	42.3	[illegible]
J3243	24.0	[illegible]

```
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

DATE: NOV 13 87
SAMPLE: J3239
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#    SIZE          DIFF       CUM
                      VOL %      VOL %
****************************************
1       1             0          100
2       1.26          .38        100
3       1.59          .48        99.62
4       2             .83        99.13
5       2.52          1.03       98.3
6       3.17          1.51       97.28
7       4             2.28       95.77
8       5.04          3.65       93.49
9       6.35          4.97       89.84
10      8             7.44       84.87
11      10.08         10.3       77.44
12      12.7          13.11      67.14
13      16            14.92      54.02
14      20.16         14.25      39.11
15      25.4          9.24       24.86
16      32            6.69       15.62
17      40.32         4.34       8.93
18      50.8          2.74       4.6
19      64            1.86       1.86
20      80.63         0          0
21      101.59        0          0
22      128           0          0


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                   16.07 UM
MEDIAN:                 17.03 UM
MODE                    18.94 UM
STANDARD DEVIATION:     2.05 UM
COEF. VAR.:             12.77 %
SKEWNESS:               .83 NEGATIVE
KURTOSIS:               2.54 PLATYKURTIC
```

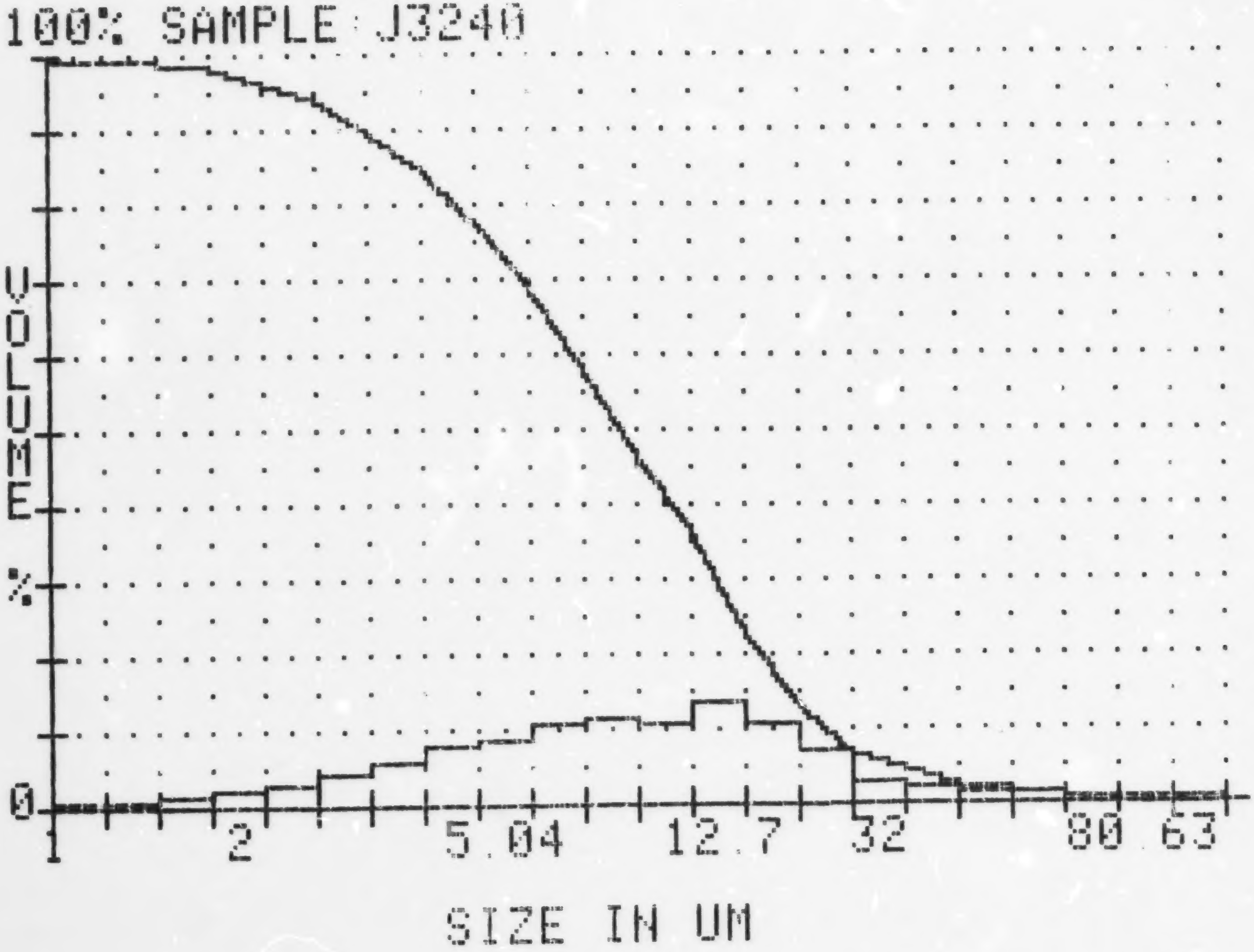

100% SAMPLE:J3239
VOLUME %
0
1
2
5.04
12.7
32
80.63
SIZE IN UM

```
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

DATE: NOV 13 87
SAMPLE: J3240
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#   SIZE          DIFF       CUM
                     VOL %      VOL %
****************************************
1      1             .49        100
2      1.26          .49        99.51
3      1.59          .93        99.02
4      2             1.83       98.09
5      2.52          2.62       96.26
6      3.17          3.72       93.63
7      4             5.41       89.92
8      5.04          7.32       84.51
9      6.35          8.52       77.19
10     8             10.65      68.67
11     10.08         11.26      58.01
12     12.7          10.76      46.76
13     16            13.17      35.99
14     20.16         10.22      22.82
15     25.4          6.52       12.61
16     32            2.26       6.09
17     40.32         2.14       3.83
18     50.8          .89        1.69
19     64            .8         .8
20     80.63         0          0
21     101.59        0          0
22     128           0          0


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                      11.19 UM
MEDIAN:                    11.88 UM
MODE                       17.75 UM
STANDARD DEVIATION:        2.16 UM
COEF. VAR.:                19.29 %
SKEWNESS:                  .86 NEGATIVE
KURTOSIS:                  2.81 PLATYKURTIC
```

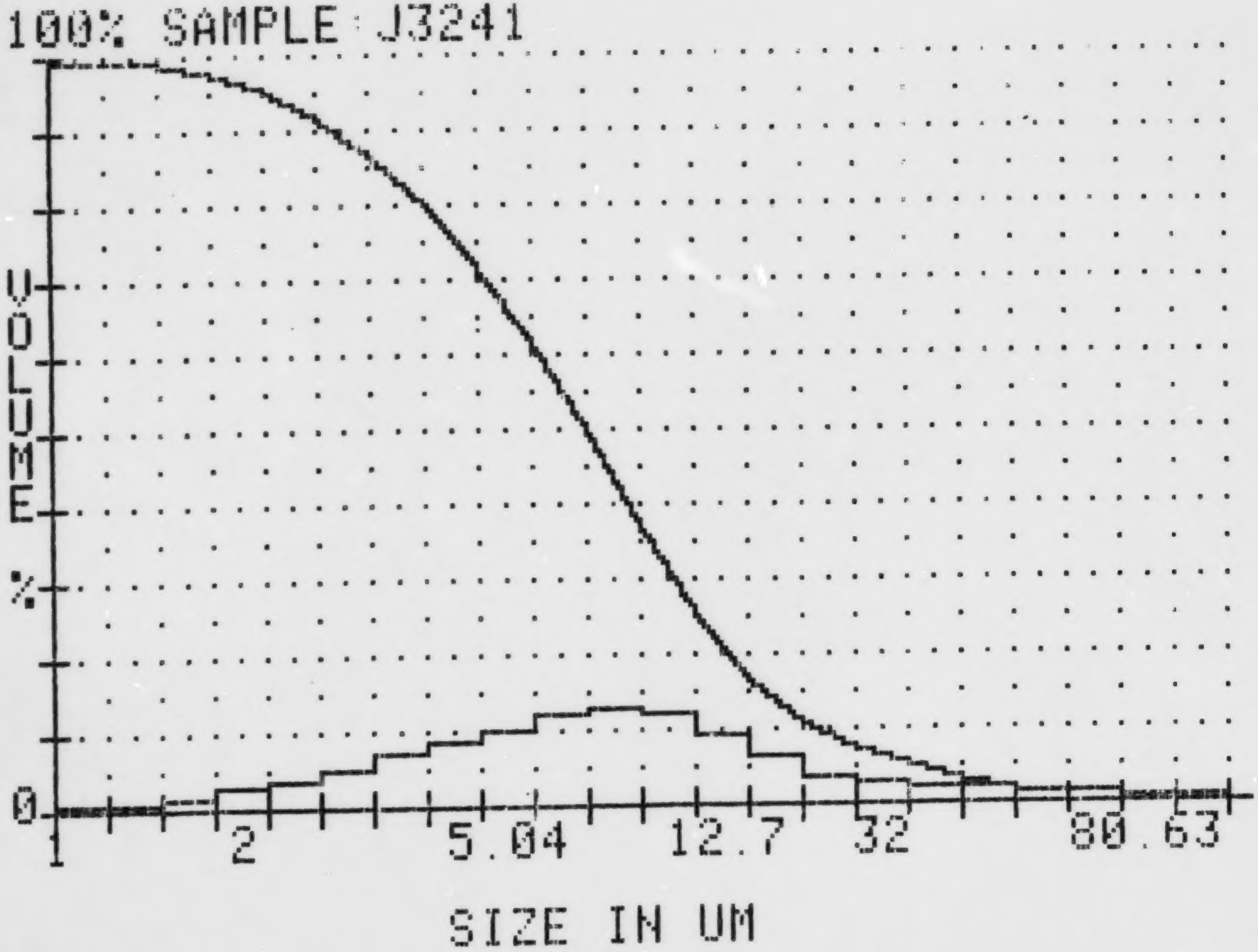

100% SAMPLE J3240
VOLUME
%
0
1
2
5.04
12.7
32
80
63
SIZE IN UM

```
 ONTARIO RESEARCH
 FINE PARTICLE LABORATORY

DATE: NOV 13 87
SAMPLE: J3241
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#   SIZE         DIFF       CUM
                    VOL %      VOL %
****************************************
1      1            .57        100
2      1.26         .65        99.43
3      1.59         1.22       98.78
4      2            2.45       97.55
5      2.52         3.42       95.1
6      3.17         4.84       91.69
7      4            6.8        86.85
8      5.04         8.62       80.05
9      6.35         9.79       71.42
10     8            11.9       61.63
11     10.08        12.75      49.73
12     12.7         11.61      36.98
13     16           9.05       25.37
14     20.16        5.92       16.32
15     25.4         3.4        10.4
16     32           2.66       7
17     40.32        2.03       4.34
18     50.8         1.56       2.31
19     64           0          .75
20     80.63        .75        .75
21     101.59       0          0
22     128          0          0


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                   9.77 UM
MEDIAN:                 10.03 UM
MODE                    11.13 UM
STANDARD DEVIATION:     2.21 UM
COEF. VAR.:             22.65 %
SKEWNESS:               1 NEGATIVE
KURTOSIS:               3.35 LEPTOKURTIC
```

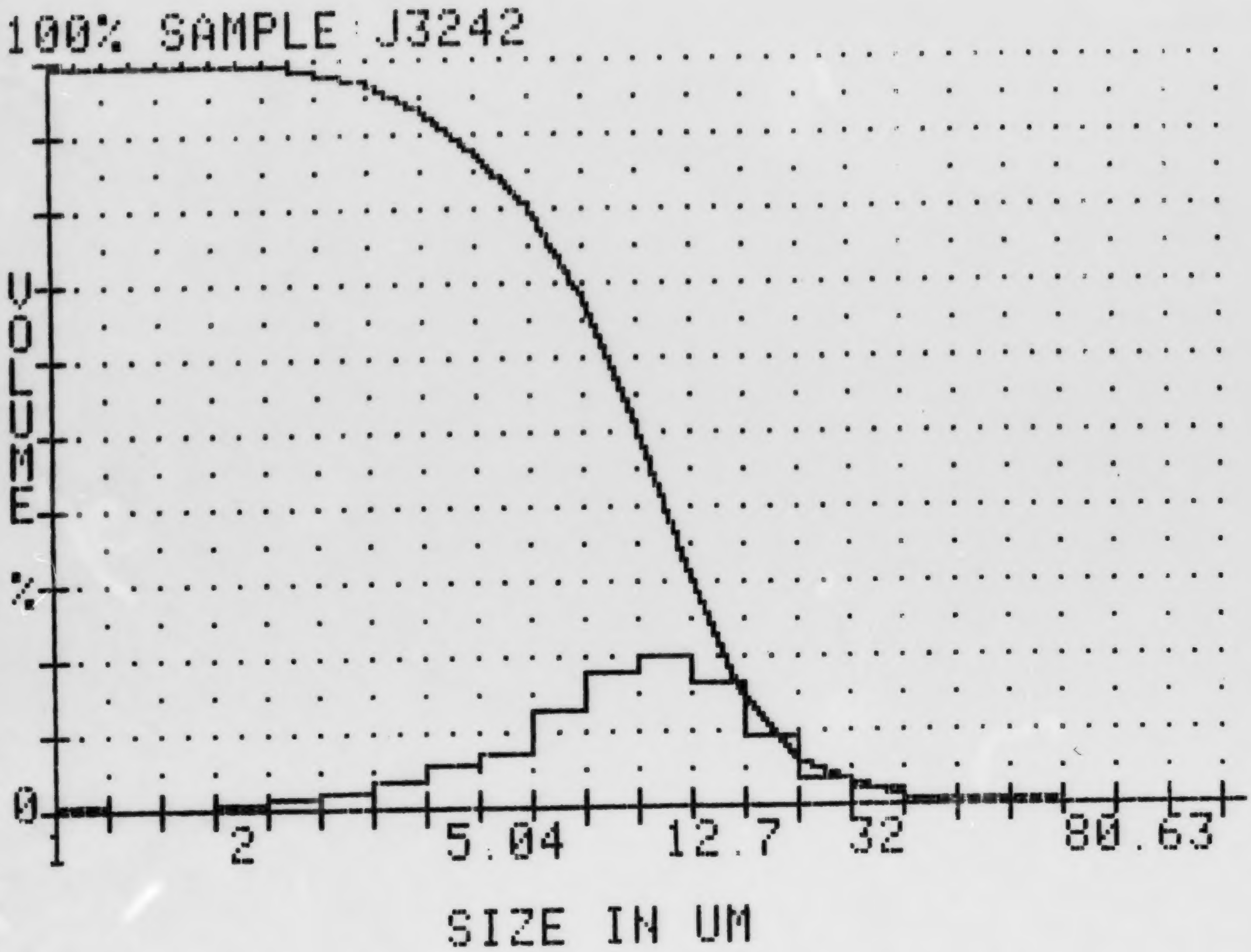

100% SAMPLE J3241
VOLUME
%
0
1
2
5.04
12.7
32
80.63
SIZE IN UM

```
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

DATE: NOV 13 87
SAMPLE: J3242
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#   SIZE         DIFF      CUM
                    VOL %     VOL %
****************************************
1      1            .22       100
2      1.26         0         99.78
3      1.59         0         99.78
4      2            .4        99.78
5      2.52         .95       99.38
6      3.17         2.01      98.43
7      4            3.58      96.42
8      5.04         5.56      92.83
9      6.35         7.17      87.27
10     8            12.45     80.11
11     10.08        17.27     67.65
12     12.7         19.92     50.39
13     16           16.27     30.47
14     20.16        8.85      14.2
15     25.4         2.96      5.35
16     32           1.7       2.39
17     40.32        .39       .69
18     50.8         .15       .31
19     64           .15       .15
20     80.63        0         0
21     101.59       0         0
22     128          0         0


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                     12 UM
MEDIAN:                   12.76 UM
MODE                      14 UM
STANDARD DEVIATION:       1.72 UM
COEF. VAR.:               14.36 %
SKEWNESS:                 .92 NEGATIVE
KURTOSIS:                 1.41 PLATYKURTIC
```

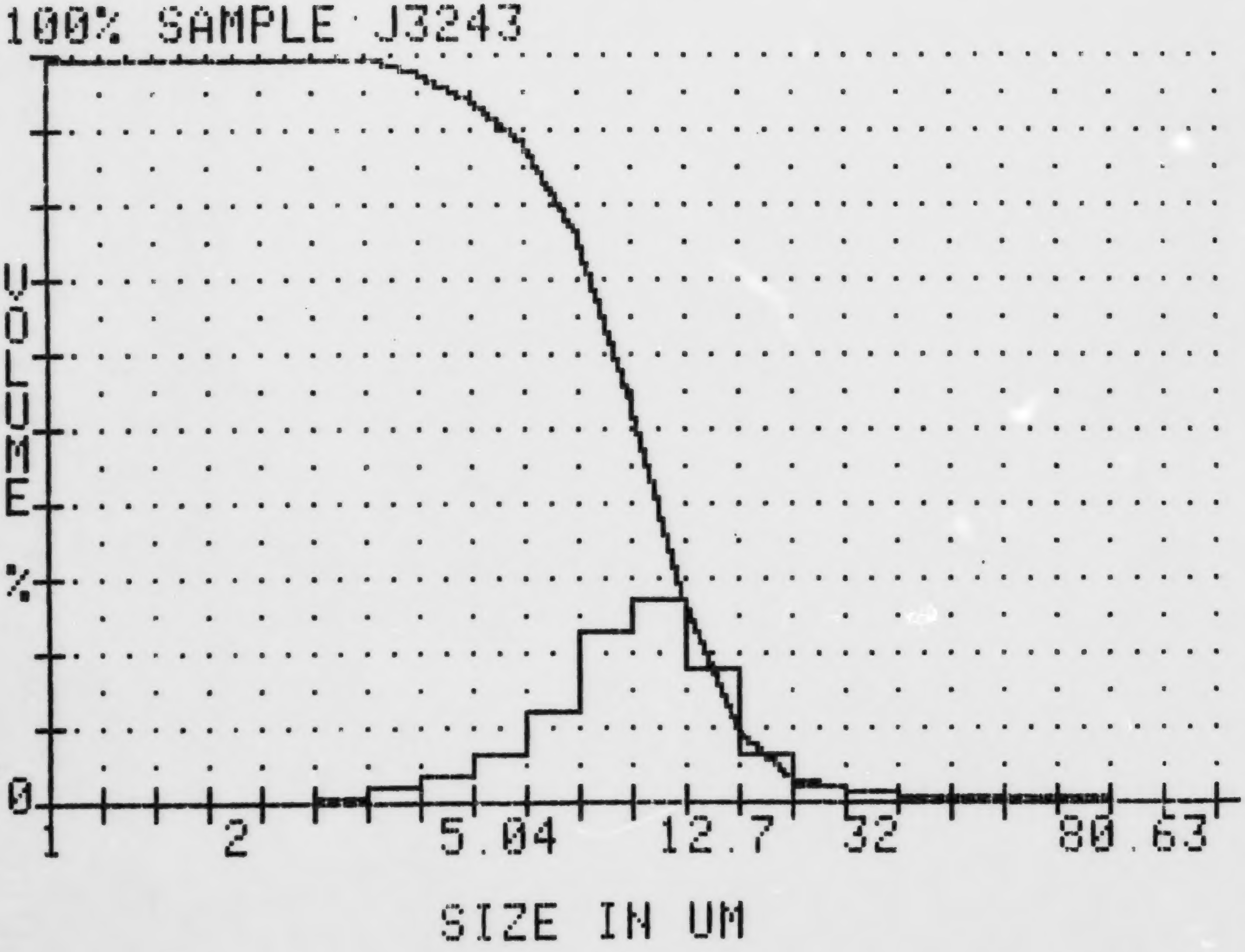

100% SAMPLE J3242
VOLUME %
0
2
5.04
12.7
32
80.63
SIZE IN UM

```
ONTARIO  RESEARCH
FINE  PARTICLE  LABORATORY

DATE: NOV 13 87
SAMPLE: J3243
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 30 SEC USB
****************************************
CH.#    SIZE            DIFF        CUM
                        VOL %       VOL %
****************************************
1       1               0           100
2       1.26            0           100
3       1.59            0           100
4       2               0           100
5       2.52            0           100
6       3.17            .71         100
7       4               2.07        99.29
8       5.04            3.54        97.23
9       6.35            5.9         93.68
10      8               11.93       87.78
11      10.08           22.56       75.85
12      12.7            27.18       53.29
13      16              17.48       26.11
14      20.16           6.08        8.64
15      25.4            1.49        2.56
16      32              .83         1.07
17      40.32           .08         .24
18      50.8            0           .16
19      64              0           .16
20      80.63           .16         .16
21      101.59          0           0
22      128             0           0


****************************************
       VOLUME % STATISTICS
****************************************

MEAN:                     12.59 UM
MEDIAN:                   13.06 UM
MODE                      13.68 UM
STANDARD DEVIATION:       1.5 UM
COEF. VAR.:               11.92 %
SKEWNESS:                 .98 NEGATIVE
KURTOSIS:                 1.12 PLATYKURTIC
```


100% SAMPLE J3243
VOLUME
%
0
1
2
5.04
12.7
32
80.63
SIZE IN UM

APPENDIX III Certificate of Analysis-Report 2969

XRAL

CERTIFICATE OF ANALYSIS

REPORT 2969

TO: ONTARIO RESEARCH FOUNDATION
ATTN: C. BOOTH
SHERIDAN PARK
MISSISSAUGA, ONTARIO
L5K 1B3

CUSTOMER No. 458

DATE SUBMITTED
12-Nov-87

REF. FILE 30310-J6

Total Pages 2

5 PULPS

	METHOD	DETECTION LIMIT
WRMAJ %	WR	0.01
WRMIN PPM	WR	10.

X-RAY ASSAY LABORATORIES LIMITED

DATE 03-DEC-87

CERTIFIED BY ....

XRF - WHOLE ROCK ANALYSIS 03-DEC-87 REPORT 2969 REFERENCE FILE 30310

SAMPLE \ %	SIO2	AL2O3	CAO	MGO	NA2O	K2O	FE2O3	MNO	TIO2	P2O5	LOI	SUM
J3239	49.0	22.6	1.78	1.20	0.25	1.38	8.62	0.17	3.11	0.15	2.23	91.2
J3240	42.7	25.3	2.12	1.38	0.67	1.80	9.36	0.20	3.53	0.22	0.93	88.6
J3241	42.1	25.5	2.34	1.37	0.65	1.80	9.33	0.20	3.52	0.24	2.47	89.9
J3242	33.4	21.1	2.33	1.07	8.04	0.97	7.93	0.17	3.13	0.20	14.7	93.3
J3243	37.4	21.9	2.10	1.20	10.5	0.38	8.48	0.20	3.25	0.20	10.5	96.4

XRF W.R.A. SUMS INCLUDE ALL ELEMENTS DETERMINED. FOR SUMMATION, ELEMENTS ARE CALCULATED AS OXIDES

?

SAMPLE \ PPM	CR	RB	SR	Y	ZR	NB	BA	✓
J3239 [illegible]	751	88	446	97	973	79	3390	
J3240 [illegible]	822	94	496	110	799	77	627	
J3241 [illegible]	822	117	482	99	794	66	565	
J3242 SOJA	378	80	390	96	807	63	513	
J3243 CA[illegible]	336	58	468	113	736	72	539	

SAMPLES WITH LOW SUMS HAVE BEEN REPEATED WITH NO CHANGE

WE HAVE CHECKED FOR THE FOLLOWING ELEMENTS:

CU, ZN, NI, PB, CO, AS, U, MO

OF WHICH NI WAS FOUND
IN GREATER THAN TRACE/MINOR QUANTITIES

THE MATRIX CORRECTION PROGRAM DOES NOT ACCOUNT FOR
THE PRESENCE OF THESE ELEMENTS

Fabrication of FCC Catalysts from Suncor Flyash Leach Residue

Progress Report #3

for

Carbovan Inc.
2200 Argentia Road
Mississauga, Ontario
L5N 2K7

Attn: Mr. Nairn McQueen

V. I. Lakshmanan
I. A. Todd
G. M. Freeman
Mineral Resources

ORF Account No. 41-10874
DSS Contract Serial No. 23440-7-9124/01-SQ

February 2, 1988

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Task 2: Specification Analysis	1
Task 3: Evaluation of Physical and Chemical Properties	2
Table 1	3
Task 4: Evaluation of Unmodified Leach Residue	3
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APPENDIX I: Mercury Porosimetry Data	5
APPENDIX II: Image Analysis Assessment of Particle Size	6

1. INTRODUCTION

In Progress Report Nos. 1 and 2, the results of Tasks 1 and 3 were briefly reported and reviewed.

In the present report, the status of Tasks 1-4 is reviewed and a summary of work completed to date is given.

Task 1: Summary

This task is complete as reported in Progress Report 1.

Task 2: Specification Analysis

A thorough review has been made of specifications of zeolite material presently in use in:

(a) F.C.C. Catalyst applications

(b) Detergent Formulation

(c) Microsieve Technology

(d) Plastics Filler Applications

From computer literature searches and from within industrial sources, representative general specification data has been obtained for application of zeolites in the above industries.

A general review of zeolite application and future trends is presently being processed and a full report will be submitted at the completion of this task.

One basic conclusion to be assessed from the survey is the extremely wide variation in zeolite products both synthetic and of natural origin. This has led to protection of proprietory zeolite products by manufacturers causing considerable reluctance to divulge the basic properties of some of their products. This is reflected in the competition for various market shares particularly in the traditional catalyst and detergent formulation areas where saturation of the market[1] has taken place.

Task 3: Evaluation of Physical and Chemical Properties

With the addition of mercury porosimetry data (Appendix I) and Image Analysis assessment of particle size (Appendix II), the physical and chemical evaluation of the basic materials will be complete. Some additional data will be obtained from N_2BET measurements which will assess the surface area and pore size present in the materials at the atomic level.

Porosimetry data and Image analysis particle size data is summarized in Table 1. In comparison to Coulter Counter data (Report #2), mean particle diameters tend to be marginally higher.

---

[1] Industrial Minerals

Paper 3 [illegible]

Table 1

Sample	Porosity (%)	Mean Pore Diameter (um)	Mean Particle Size (um) by mass [illegible]
BHA Float Tailing	51.6	0.145	21
ESP Float Tailing	45.4	0.113	18
3:1 ESP/BHA Float Tailing	45.6	0.079	11
NaOH Leach Tailing	75.0	0.104	14
$NaOH/Na_2CO_3$ Leach Tailing	68.0	0.118	13

Task 4: Evaluation of Unmodified Leach Residue

As a precursor to the above task, a large batch sample of NaOH leach tailings was prepared. This material was then thoroughly blended, prior to sampling for testing potential areas of use. A representative portion of the material is presently being assayed and basic physical properties assessed to ensure continuity with previous work.

Sample 1 - 250 g has been sent to SRC for catalyst evaluation.

Sample 2 - 2 kgs is being compounded with polypropylene for filler application assessment.

Sample 3 - 100 g is under test for detergent formulation applications

Sample 4 - 250 g is under test for Microsieve activity.

A full report will be submitted as soon as this task is complete.

Task Completion Summary

Task 1	Summary	Complete
Task 2	Specification Analysis	90% Complete
Task 3	Evaluate Physical and Chemical Properties	90% Complete
Task 4	Evaluate Unmodified Leach Residue	50% Complete

V. I. Lakshmanan
Project Manager
Mineral Resources

G. M. Freeman
Operations Manager
Mineral Resources

I. A. Todd
Project Scientist
Mineral Resources

APPENDIX I: Mercury Porosimetry Data

```
[illegible]                                                [illegible] 10/19/87
                                                           [illegible]
[illegible]

 EQUILIBRATION [illegible]    [illegible] SEC         PNTR CONSTANT =  +27.8200 [illegible]
 EVACUATION [illegible]       [illegible]                     THETA =  +1[illegible]
   SAMPLE WEIGHT =       [illegible].3000 G                   GAMMA =  +485.0000 DYNES/CM
     PNTR WEIGHT =    +[illegible].7700 G        INITIAL PRESSURE =    +0.3483 PSIA
PNTR+SAMPLE WEIGHT =    +70.0300 G                  PORE DIAMETER =  +528.1340 MICRO-M
PNTR+SAMPLE+MERCURY =  +[illegible].4000 G        MERCURY DENSITY =   +13.5338 G/CC
     PNTR VOLUME =      +3.[illegible] CC


INTRUSION (PRESSURIZATION) DATA SUMMARY

       TOTAL INTRUSION VOLUME =     +0.4345 CC/G
              TOTAL PORE AREA =    +12.0077 SQ-M/G
MEDIAN PORE DIAMETER  (VOLUME) =    +3.2251 MICROMETERS
MEDIAN PORE DIAMETER  (AREA)   =    +0.0058 MICROMETERS
AVERAGE PORE DIAMETER (4V/A)   =    -0.1448 MICROMETERS
                 BULK DENSITY =     +1.1884 G/CC
APPARENT (SKELETAL) DENSITY =       +2.4575 G/CC

% CAPILLARY =  +40.38[illegible]
```

5 µ

% POROSITY = 51.6

[illegible] PARTICLE LAB   [illegible] 07/13/87
[illegible] 07/13/87

PRESSURE PSIA	PORE DIAMETER MICRON	INTRUSION VOLUME CC/G	PORE SURFACE SQ-M/G	MEAN DIAMETER MICRON	DV
+0.5	+324.8830	+0.0000	+0.0000	+328.8880	+0.0000
+1.0	+178.8840	+0.0027	+0.0000	+231.8830	+0.0027
+2.0	+90.4854	+0.0137	+0.0008	+133.3880	+0.0170
+3.0	+58.2012	+0.0324	+0.0012	+74.0581	+0.0127
+4.0	+43.1312	+0.0340	+0.0014	+52.3817	+0.0015
+5.0	+33.1454	+0.0382	+0.0018	+40.3386	+0.0042
+6.0	+30.1801	+0.0413	+0.0021	+33.1327	+0.0031
+7.0	+25.8777	+0.0440	+0.0025	+28.0285	+0.0027
+8.0	+22.3488	+0.0471	+0.0030	+24.2383	+0.0031
+9.0	+20.1330	+0.0502	+0.0036	+21.3827	+0.0031
+10.0	+18.1824	+0.0537	+0.0043	+19.1444	+0.0035
+11.5	+15.1383	+0.0564	+0.0050	+16.3444	+0.0027
+13.5	+12.8805	+0.0587	+0.0057	+14.0[illegible]	+0.0023
+15.5	+11.2787	+0.0614	+0.0065	+12.[illegible]	+0.0027
+18.0	+10.0841	+0.0641	+0.0075	+10.7088	+0.0027
+20.5	+8.8082	+0.0656	+0.0082	+9.5802	+0.0015
+24.5	+7.283	+0.0707	+0.0107	+8.1575	+0.0050
+35.8	+5.2311	+0.0707	+0.0107	+3.7725	+0.0000
+38.3	+4.3827	+0.0811	+0.0183	+5.4884	+0.0104
+47.2	+3.7821	+0.1372	+0.0555	+4.2374	+0.0561
+58.0	+3.1203	+0.2236	+0.1384	+3.4315	+0.0865
+72.8	+2.4811	+0.2737	+0.2365	+2.8010	+0.0480
+87.5	+1.8841	+0.3132	+0.3133	+2.1879	+0.0408
+122.3	+1.4750	+0.3375	+0.3343	+1.8866	+0.0213
+147.2	+1.2288	+0.3507	+0.4032	+1.3538	+0.0132
+172.1	+1.0511	+0.3588	+0.4344	+1.1388	+0.0088
+198.8	+0.9028	+0.3663	+0.4528	+0.9804	+0.0070
+247.3	+0.7303	+0.3770	+0.5140	+0.8202	+0.0105
+298.8	+0.3033	+0.3848	+0.5304	+0.6887	+0.0078
+398.4	+0.4522	+0.3910	+0.6076	+0.5311	+0.0063
+497.1	+0.3678	+0.3954	+0.6501	+0.4084	+0.0043
+598.3	+0.3021	+0.3974	+0.6743	+0.3330	+0.0020
+745.1	+0.2427	+0.3997	+0.7100	+0.2724	+0.0024
+995.1	+0.1817	+0.4031	+0.7715	+0.2122	+0.0033
+1247.2	+0.1450	+0.4048	+0.8131	+0.1634	+0.0017
+1493.3	+0.1211	+0.4065	+0.8336	+0.1331	+0.0017
+1990.3	+0.0908	+0.4083	+0.9307	+0.1060	+0.0018
+2975.7	+0.0608	+0.4108	+1.0712	+0.0758	+0.0027
+4980.0	+0.0362	+0.4141	+1.3287	+0.0485	+0.0031
+7468.3	+0.0242	+0.4157	+1.3756	+0.0303	+0.0023
+9937.2	+0.0182	+0.4188	+2.0735	+0.0212	+0.0021
+14972.4	+0.0121	+0.4237	+3.5213	+0.0135	+0.0048
+19961.2	+0.0091	+0.4273	+5.3047	+0.0078	+0.0036
+29781.1	+0.0045	+0.4307	+7.8432	+0.0053	+0.0031
+44850.0	+0.0030	+0.4330	+10.1918	+0.0041	+0.0023
+59745.0	+0.0030	+0.4345	+12.0077	+0.0030	+0.0015
+45805.3	+0.0033	+0.4345	+12.0077	+0.0033	+0.0000
+40[illegible].0	+0.0043	+0.4345	+12.0077	+0.0041	+0.0000

```
[illegible]                                                         [illegible] .2/13/37
                                                                    [illegible] 2/77
[illegible]

[illegible]          [illegible]          [illegible]          [illegible]          [illegible]
                                                    SG-Y/S

 -30002.2          +0.0080          +0.4343          +12.0077          -0.0053          +0.0000
 -20000.3          -0.0050          +0.4343          +11.5513          +0.0075          -0.0000
 -10000.?          -0.0130          +0.4318          +11.2155          -0.0133          -0.0025
  -7502.?          -0.0240          +0.43[illegible]  +11.0376          -0.0210          -0.0010
  -5002.7          -0.0381          +0.4281          +10.7818          +0.0301          -0.0018
  -2500.2          -0.0722          -0.4232          +10.3774          -0.0542          -0.0025
  -1000.6          -0.1302          +0.4232          +10.4614          -0.1230          -0.0030
   -745.8          +0.2412          +0.4222          +10.4633          -0.2107          -0.0010
   -485.3          +0.3318          +0.4216          +10.4555          -0.3015          -0.0003
   -248.0          +0.7238          +0.4202          +10.4453          -0.5444          -0.0014
    +87.3          +1.5345          +0.4182          +10.4388          +1.2807          -0.0021
    -73.0          -2.4751          +0.4177          +10.4380          +2.1553          -0.0004
    +47.3          +3.7734          +0.4185          +10.4370          -3.1373          -0.0005
    -24.7           7.4730          +0.4134          +10.4353          +5.3343          -0.0013
```

[illegible] LAB [illegible]

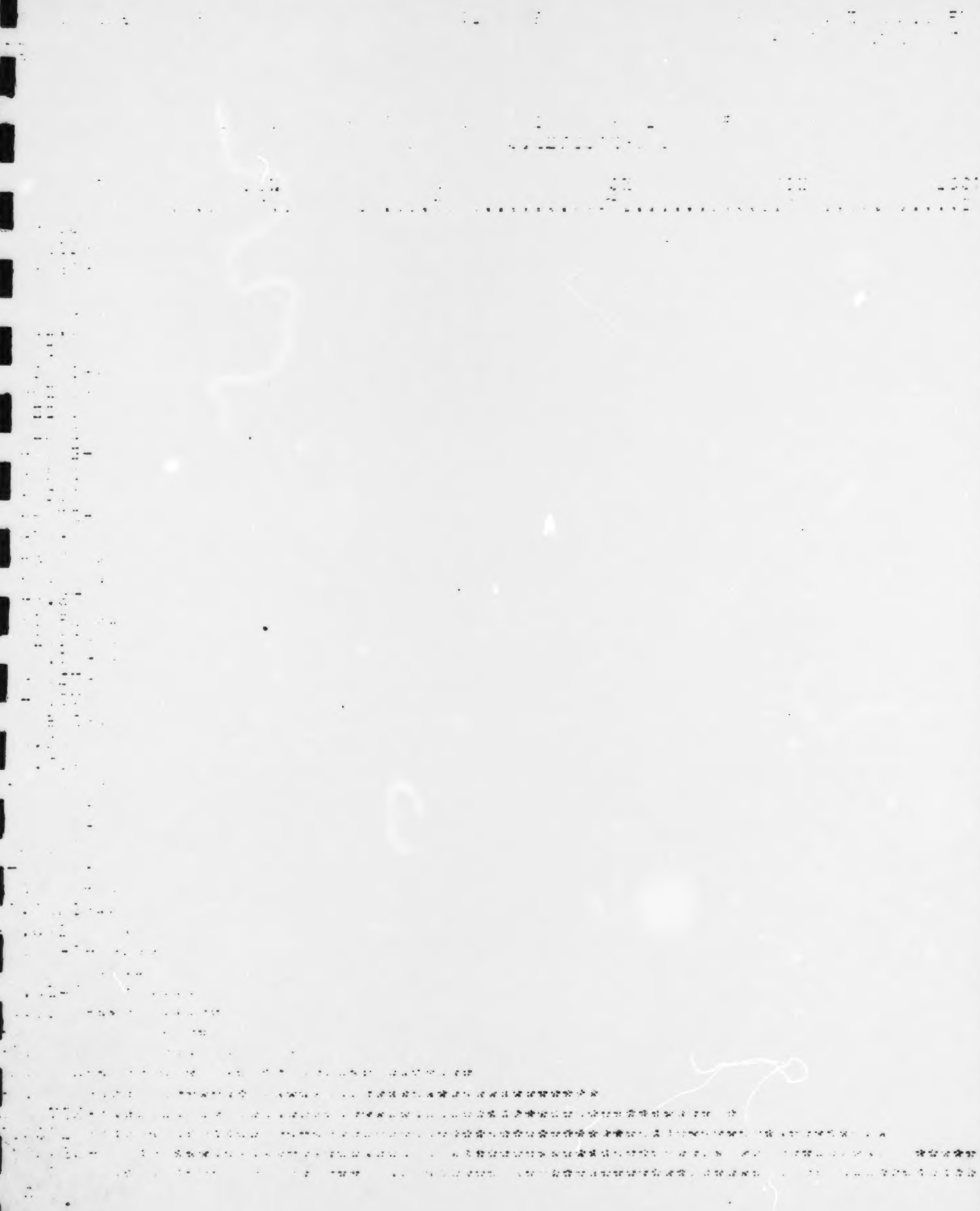
[illegible]

CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER
100% = -0.4345

```
[illegible]                                                    [illegible]
[illegible]                                                    [illegible]
[illegible] NUMBER [illegible]-3

             [illegible] SURFACE AREA [illegible]2/G) VS. PORE DIAMETER
                              100% =     +12.0077

         0%           20%          40%          60%          80%          100%
          I............I............I............I............I............I
    -[illegible]-*
      +205-*
      +134-*
      +144-*
    -[illegible]-*
     +80.1-*
     +65.0-*
     +54.0-*
     +41.3-*
     +33.1-*
     +29.5-*
     +20.0-*
     +15.8-*
     +12.4-*
     +8.72-*
     +7.31-*
     +5.55-*
     +4.33-*
     +3.35-*
     +2.85-*
     +2.24- *
     +1.75- *
     +1.37- *
     +1.07-  *
    -0.833-  *
    +0.557-  *
    +0.514-  *
    +0.402-   *
    -0.313-   *
    -0.247-   *
    -0.180-   *
    +0.151-    *
    +0.116-    *
   +0.0823-    *
   -0.0725-     *
   +0.0557-     *
   +0.0444-      *
   -0.0347-       *
   +0.0272-        *
   +0.0213-          *
   -0.0137-
   +0.0130-              *
   +0.0102-                *
  -0.00755-                     *
  +0.00523-                           *
  +0.00450-                                      *
  +0.00355-                                                 *
  +0.00300-                                                              #
```



SAMPLE J3240

```
NTARIO RESEARCH FINE PARTICLE LAB                                    LP 9:43:55 12/17/87
3240                                                                 HP 10:11:3 12/17/87
PNTR NUMBER  +158

   LP EGUILIBRATION =    +30.0000 SEC          PNTR CONSTANT =    +27.8200 MICRO-L/PF
   HP EGUILIBRATION =    +30.0000 SEC                  THETA =   +130.0000
      SAMPLE WEIGHT =     +1.5200 G                    GAMMA =   +485.0000 DYNES/CM
        PNTR WEIGHT =    +69.6300 G         INITIAL PRESSURE =     +0.5275 PSIA
 PNTR+SAMPLE WEIGHT =    +71.1500 G            PORE DIAMETER =   +342.8750 MICRO-M
PNTR+SAMPLE+MERCURY =   +144.7600 G          MERCURY DENSITY =    +13.5335 G/CC
        PNTR VOLUME =     +6.6177 CC



INTRUSION (PRESSURIZATION) DATA SUMMARY

         TOTAL INTRUSION VOLUME =     +0.3521 CC/G
                TOTAL PORE AREA =    +12.4476 SG-M/G
MEDIAN PORE DIAMETER  (VOLUME) =     +1.5956 MICROMETERS
MEDIAN PORE DIAMETER  (AREA)   =     +0.0057 MICROMETERS
  AVERAGE PORE DIAMETER (4V/A) =     +0.1132 MICROMETERS
                  BULK DENSITY =     +1.2897 G/CC
    APPARENT (SKELETAL) DENSITY =     +2.3627 G/CC

% CAPILLARY =  +30.3611
```

% POROSITY = 45.4

```
ON ARIO RESEARCH FINE PARTICLE LAB                                      LP 9:43:55 12/17/87
J3240                                                                   HP 10:11:3 12/17/87
PN R NUMBER   +158

 PRESSURE        PORE          INTRUSION        PORE          MEAN
   PSIA        DIAMETER          VOLUME        SURFACE       DIAMETER          DV
                MICRG-M           CC/G          SG-M/G        MICRO-M

      +0.5     +338.1820        +0.0000        +0.0000      +340.5310       +0.0000
      +1.0     +176.3380        +0.0036        +0.0001      +257.2600       +0.0036
      +2.0      +92.1169        +0.0201        +0.0005      +134.2270       +0.0165
      +3.0      +61.2589        +0.0286        +0.0010       +76.6878       +0.0085
      +4.0      +44.8860        +0.0362        +0.0016       +53.0724       +0.0076
      +4.9      +36.6281        +0.0425        +0.0022       +40.7570       +0.0063
      +6.0      +30.1432        +0.0483        +0.0029       +33.3856       +0.0058
      +6.9      +26.1242        +0.0483        +0.0029       +28.1337       +0.0000
      +8.0      +22.6905        +0.0501        +0.0032       +24.4073       +0.0018
      +9.0      +20.1201        +0.0505        +0.0033       +21.4053       +0.0004
     +10.0      +18.1391        +0.0519        +0.0035       +19.1296       +0.0013
     +12.0      +15.0993        +0.0550        +0.0043       +16.6192       +0.0031
     +13.9      +12.9660        +0.0586        +0.0053       +14.0326       +0.0036
     +15.9      +11.3609        +0.0608        +0.0060       +12.1635       +0.0022
     +17.9      +10.0971        +0.0622        +0.0065       +10.7290       +0.0013
     +20.0       +9.0596        +0.0644        +0.0075        +9.5783       +0.0022
     +25.0       +7.2461        +0.0684        +0.0095        +8.1528       +0.0040
     +28.5       +6.3392        +0.0685        +0.0095        +6.7926       +0.0001
     +38.5       +4.6984        +0.0685        +0.0095        +5.5188       +0.0000
     +48.4       +3.7332        +0.0712        +0.0121        +4.2158       +0.0027
     +58.7       +3.0812        +0.0725        +0.0136        +3.4072       +0.0014
     +73.6       +2.4587        +0.0752        +0.0175        +2.7700       +0.0027
     +98.5       +1.8369        +0.1338        +0.1267        +2.1478       +0.0586
    +122.9       +1.4717        +0.1978        +0.2813        +1.6543       +0.0639
    +147.8       +1.2234        +0.2282        +0.3716        +1.3475       +0.0304
    +172.9       +1.0458        +0.2524        +0.4568        +1.1346       +0.0242
    +199.1       +0.9083        +0.2662        +0.5139        +0.9771       +0.0139
    +247.7       +0.7302        +0.2855        +0.6077        +0.8193       +0.0193
    +299.4       +0.6041        +0.2909        +0.6402        +0.6672       +0.0054
    +399.0       +0.4533        +0.2924        +0.6512        +0.5287       +0.0014
    +497.7       +0.3634        +0.2943        +0.6697        +0.4083       +0.0019
    +597.3       +0.3028        +0.2944        +0.6709        +0.3331       +0.0001
    +748.6       +0.2416        +0.3204        +1.0539        +0.2722       +0.0261
    +997.7       +0.1813        +0.3256        +1.1507        +0.2114       +0.0051
   +1246.7       +0.1451        +0.3262        +1.1661        +0.1632       +0.0006
   +1495.8       +0.1209        +0.3264        +1.1709        +0.1330       +0.0002
   +1988.1       +0.0910        +0.3275        +1.2147        +0.1059       +0.0012
   +2989.1       +0.0605        +0.3284        +1.2598        +0.0757       +0.0009
   +4980.5       +0.0363        +0.3329        +1.6335        +0.0484       +0.0045
   +7484.1       +0.0242        +0.3355        +1.9755        +0.0302       +0.0026
   +9957.8       +0.0182        +0.3370        +2.2679        +0.0212       +0.0015
  +19957.1       +0.0091        +0.3405        +3.2868        +0.0136       +0.0035
  +29866.9       +0.0061        +0.3450        +5.6978        +0.0076       +0.0046
  +39970.5       +0.0045        +0.3477        +7.7341        +0.0053       +0.0027
  +49865.5       +0.0036        +0.3504       +10.3446        +0.0041       +0.0027
  +59730.6       +0.0030        +0.3521       +12.4476        +0.0033       +0.0017
  +49910.2       +0.0036        +0.3521       +12.4476        +0.0033       +0.0000
  +40179.1       +0.0045        +0.3518       +12.0665        +0.0041       -0.0004
```

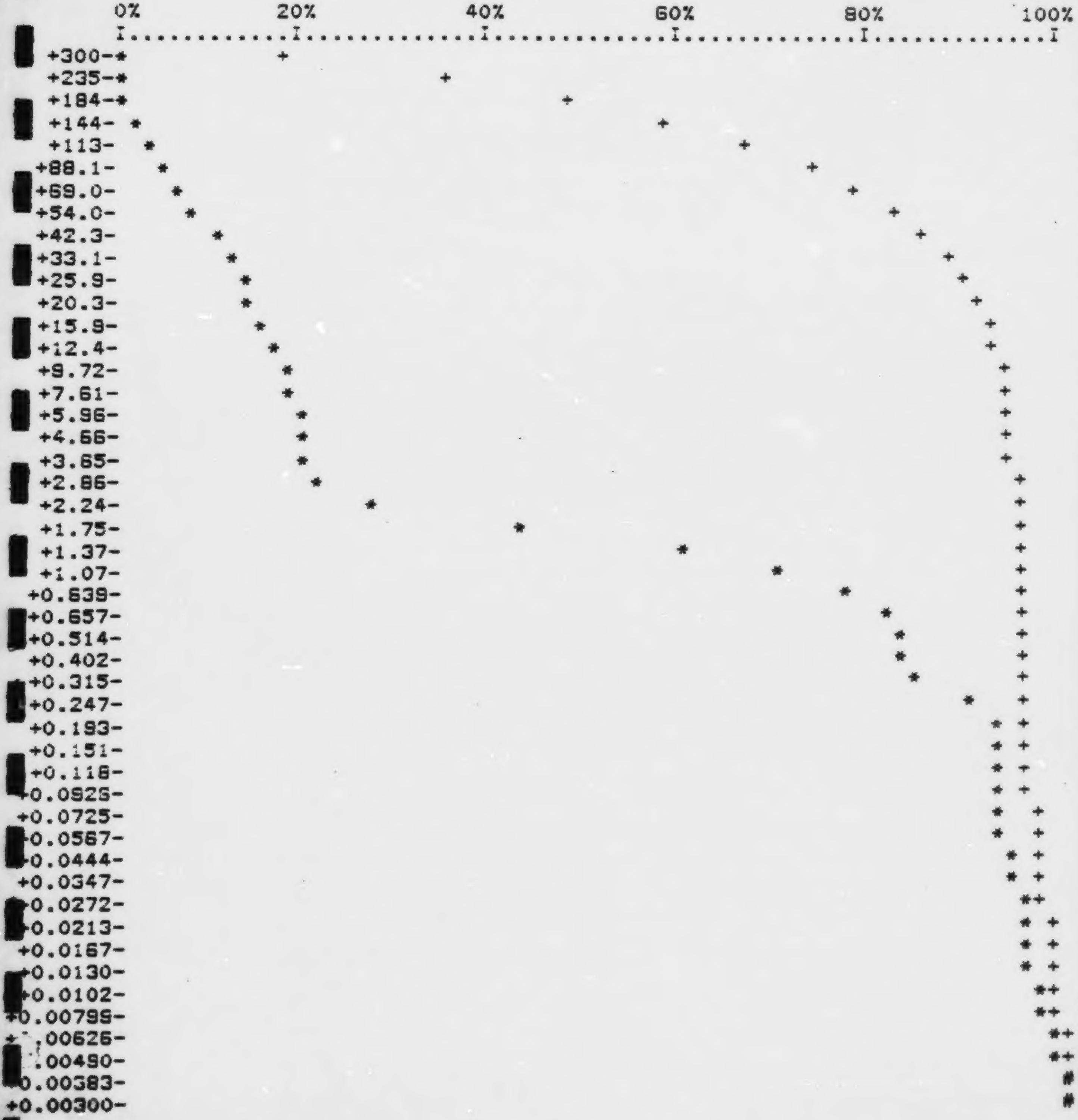
```
NT RIO RESEARCH FINE PARTICLE LAB
3240                                                                    LP 9:43:55 12/17/87
N[illegible] NUMBER  +158                                               HP 10:11:13 12/17/87

 PRESSURE        PORE         INTRUSION        PORE          MEAN
   PSIA        DIAMETER        VOLUME         SURFACE       DIAMETER          DV
               MICRO-M          CC/G          SQ-M/G        MICRO-M

 +30030.8      +0.0060        +0.3504        +11.0392       +0.0053        -0.0014
 +20091.2      +0.0090        +0.3481         +9.8039       +0.0075        -0.0023
 +10047.2      +0.0180        +0.3451         +8.9101       +0.0135        -0.0030
  +7543.6      +0.0240        +0.3444         +8.7857       +0.0210        -0.0007
  +5010.3      +0.0361        +0.3427         +8.5603       +0.0300        -0.0017
  +2572.4      +0.0703        +0.3398         +8.3430       +0.0532        -0.0029
  +1004.4      +0.1801        +0.3376         +8.2727       +0.1252        -0.0022
   +750.5      +0.2410        +0.3370         +8.2603       +0.2105        -0.0007
   +498.5      +0.3628        +0.3367         +8.2572       +0.3019        -0.0002
   +246.4      +0.7281        +0.3356         +8.2486       +0.5454        -0.0012
    +99.8      +1.8124        +0.3350         +8.2467       +1.2702        -0.0006
    +74.4      +2.4294        +0.3349         +8.2466       +2.1209        -0.0000
    +50.0      +3.6188        +0.3344         +8.2460       +3.0241        -0.0005
    +24.9      +7.2776        +0.3340         +8.2456       +5.4482        -0.0005
```

```
ONTARIO RESEARCH FINE PARTICLE LAB                    LP 9:43:55 12/17/87
3240                                                  HP 10:11:3 12/17/87
PNTR NUMBER   +158
```

CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER
100% = +0.3521



```
ONTARIO RESEARCH FINE PARTICLE LAB                     LP 9:43:55 12/17/87
J3240                                                  HP 10:11:3 12/17/87
PN R NUMBER   +158

             CUMULATIVE SURFACE AREA (M2/G) VS. PORE DIAMETER
                                100% =    +12.4476

        0%          20%          40%          60%          80%          100%
         I............I............I............I............I............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +88.1-*
   +69.0-*
   +54.0-*
   +42.3-*
   +33.1-*
   +25.9-*
   +20.3-*
   +15.9-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-*
   +1.75-*
   +1.37- *
   +1.07- *
  +0.839-  *
  +0.657-   *
  +0.514-   *
  +0.402-   *
  +0.315-   *
  +0.247-     *
  +0.193-     *
  +0.151-      *
  +0.118-      *
 +0.0926-      *
 +0.0725-      *
 +0.0567-      *
 +0.0444-       *
 +0.0347-        *
 +0.0272-          *
 +0.0213-           *
 +0.0167-             *
 +0.0130-               *
 +0.0102-                 *
+0.00795-                      *
  .00626-                             *
  .00490-                                       *
+0.00383-                                                    *
+0.00300-                                                                  #
```

```
ONTARIO RESEARCH FINE PARTICLE LAB                         LP 9:43:55 12/17/87
 3240                                                      HP 10:11:3 12/17/87
PNTR NUMBER  +156


                  INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                  100% = +0.598574E-001

         0%          20%           40%           60%           80%          100%
         I............I.............I.............I.............I.............I
    +300-*
    +235-***
    +184-****
    +144-**********
    +113-****************
   +88.1-******************
   +69.0-************
   +54.0-*********
   +42.3-********
   +33.1-*******
   +25.9-*
   +20.3-*
   +15.9-***
   +12.4-****
   +9.72-**
   +7.61-****
   +5.96-*
   +4.66-*
   +3.65-***
   +2.86-**
   +2.24-***************************
   +1.75-**********************************************************************
   +1.37-***********************************************************
   +1.07-*****************************
  +0.839-*******************
  +0.657-*************
  +0.514-****
  +0.402-**
  +0.315-*
  +0.247-****************************
  +0.193-***********
  +0.151-**
  +0.118-*
 +0.0926-*
 +0.0725-*
 +0.0567-**
 +0.0444-****
 +0.0347-*****
 +0.0272-****
 +0.0213-**
 +0.0167-**
 +0.0130-***
 +0.0102-****
+0.00799-*****
+0.00626-*****
+0.00490-****
+0.00383-***
+0.00300-*
```

```
NTARIO RESEARCH FINE PARTICLE LAB                                    LP 9:43:55 12/17/87
3240                                                                 HP 10:11:3 12/17/87
PNTR NUMBER   +158


                  INCREMENTAL SURFACE AREA (M2/G) VS. DIAMETER
                                100% = +0.247909E+001

           0%           20%           40%           60%           80%          100%
           I............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +88.1-*
   +69.0-*
   +54.0-*
   +42.3-*
   +33.1-*
   +25.9-*
   +20.3-*
   +15.9-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-*
   +1.75-***
   +1.37-****
   +1.07-**
  +0.839-**
  +0.657-**
  +0.514-*
  +0.402-*
  +0.315-*
  +0.247-**********
  +0.193-****
  +0.151-*
  +0.118-*
 +0.0926-*
 +0.0725-*
 +0.0567-***
 +0.0444-*******
 +0.0347-**********
 +0.0272-**********
 +0.0213-*********
 +0.0167-************
 +0.0130-********************
 +0.0102-**************************
+0.00799-*******************************************
+0.00626-*****************************************************************
+0.00450-************************************************************
+0.00383-**********************************************************************
 0.00300-*
```

SAMPLE J3241

```
ONTARIO RESEARCH FINE PARTICLE LAB                                   LP 9:43:55 12/17/87
J3241                                                                HP 10:11:3 12/17/87
PNTR NUMBER   +145

   LP EQUILIBRATION =   +30.0000 SEC        PNTR CONSTANT =   +27.8200 MICRO-L/PF
   HP EQUILIBRATION =   +30.0000 SEC                THETA =  +130.0000
      SAMPLE WEIGHT =    +1.5100 G                  GAMMA =  +485.0000 DYNES/CM
        PNTR WEIGHT =   +68.8100 G       INITIAL PRESSURE =    +0.5275 PSIA
 PNTR+SAMPLE WEIGHT =   +70.3200 G          PORE DIAMETER =  +342.8790 MICRO-M
PNTR+SAMPLE+MERCURY =  +146.7500 G        MERCURY DENSITY =   +13.5335 G/CC
        PNTR VOLUME =    +6.7176 CC


INTRUSION (PRESSURIZATION) DATA SUMMARY

        TOTAL INTRUSION VOLUME =    +0.3234 CC/G
               TOTAL PORE AREA =   +16.3597 SQ-M/G
MEDIAN PORE DIAMETER  (VOLUME) =    +1.2955 MICROMETERS
MEDIAN PORE DIAMETER  (AREA)   =    +0.0055 MICROMETERS
  AVERAGE PORE DIAMETER (4V/A) =    +0.0791 MICROMETERS
                  BULK DENSITY =    +1.4110 G/CC
  APPARENT (SKELETAL) DENSITY =    +2.5952 G/CC

% CAPILLARY =  +27.6967
```

% POROSITY = 45.6

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NTARIO RESEARCH FINE PARTICLE LAB                                        LP 9:43:55 12/17/87
3241                                                                     HP 10:11:3 12/17/87
NT[illegible] NUMBER   +145

 PRESSURE        PORE         INTRUSION        PORE          MEAN
   PSIA        DIAMETER        VOLUME        SURFACE       DIAMETER            DV
               MICRO-M          CC/G          SG-M/G        MICRO-M

     +0.5     +338.1820       +0.0000        +0.0000      +340.5310         +0.0000
     +1.0     +176.3380       +0.0090        +0.0001      +257.2600         +0.0090
     +2.0      +92.1169       +0.0234        +0.0006      +134.2270         +0.0144
     +3.0      +61.2589       +0.0346        +0.0012       +76.6878         +0.0112
     +4.0      +44.8660       +0.0436        +0.0018       +53.0724         +0.0090
     +4.9      +36.6281       +0.0445        +0.0019       +40.7570         +0.0009
     +6.0      +30.1432       +0.0468        +0.0022       +33.3856         +0.0023
     +6.9      +26.1242       +0.0477        +0.0023       +26.1337         +0.0009
     +8.0      +22.6905       +0.0504        +0.0028       +24.4073         +0.0027
     +9.0      +20.1201       +0.0527        +0.0032       +21.4053         +0.0023
    +10.0      +18.1391       +0.0545        +0.0036       +19.1296         +0.0018
    +12.0      +15.0993       +0.0576        +0.0043       +16.6192         +0.0032
    +13.9      +12.9660       +0.0594        +0.0048       +14.0326         +0.0018
    +15.9      +11.3609       +0.0612        +0.0054       +12.1635         +0.0018
    +17.9      +10.0971       +0.0635        +0.0063       +10.7290         +0.0023
    +20.0       +9.0596       +0.0644        +0.0066        +9.5783         +0.0009
    +25.0       +7.2461       +0.0684        +0.0086        +8.1528         +0.0041
    +28.5       +6.3388       +0.0684        +0.0086        +6.7924         +0.0000
    +38.5       +4.6980       +0.0684        +0.0086        +5.5184         +0.0000
    +48.5       +3.7328       +0.0702        +0.0104        +4.2154         +0.0018
    +58.7       +3.0809       +0.0716        +0.0120        +3.4068         +0.0014
    +73.6       +2.4584       +0.0730        +0.0139        +2.7696         +0.0014
    +98.7       +1.8325       +0.0735        +0.0148        +2.1454         +0.0005
   +123.1       +1.4688       +0.1374        +0.1697        +1.6506         +0.0639
   +148.1       +1.2216       +0.1721        +0.2728        +1.3452         +0.0347
   +173.2       +1.0445       +0.1991        +0.3683        +1.1330         +0.0270
   +199.3       +0.9075       +0.2185        +0.4477        +0.9760         +0.0194
   +247.8       +0.7297       +0.2460        +0.5821        +0.8186         +0.0275
   +299.5       +0.6039       +0.2604        +0.6688        +0.6668         +0.0145
   +399.1       +0.4532       +0.2713        +0.7513        +0.5285         +0.0109
   +497.7       +0.3634       +0.2764        +0.8008        +0.4083         +0.0051
   +597.4       +0.3028       +0.2801        +0.8452        +0.3331         +0.0037
   +748.7       +0.2416       +0.2834        +0.8936        +0.2722         +0.0033
   +997.8       +0.1813       +0.2876        +0.9741        +0.2114         +0.0043
  +1246.9       +0.1450       +0.2896        +1.0226        +0.1632         +0.0020
  +1496.0       +0.1209       +0.2907        +1.0545        +0.1330         +0.0011
  +1988.3       +0.0910       +0.2918        +1.0987        +0.1059         +0.0012
  +2989.2       +0.0605       +0.2940        +1.2153        +0.0757         +0.0022
  +4980.7       +0.0363       +0.2968        +1.4428        +0.0484         +0.0028
  +7484.2       +0.0242       +0.2994        +1.7870        +0.0302         +0.0026
  +9958.0       +0.0182       +0.3014        +2.1664        +0.0212         +0.0020
 +19957.2       +0.0091       +0.3080        +4.1176        +0.0136         +0.0066
 +29667.1       +0.0061       +0.3131        +6.7827        +0.0076         +0.0050
 +39970.7       +0.0045       +0.3180       +10.5333        +0.0053         +0.0050
 +49865.6       +0.0036       +0.3207       +13.1612        +0.0041         +0.0027
 +59730.8       +0.0030       +0.3234       +16.3597        +0.0033         +0.0027
 +49910.3       +0.0036       +0.3234       +16.3597        +0.0033         +0.0000
 +40179.3       +0.0045       +0.3234       +16.3597        +0.0041         +0.0000
```

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ONTARIO RESEARCH FINE PARTICLE LAB                                    LP 9:43:55 12/17/87
J3241                                                                 HP 10:11:3 12/17/87
PNTR NUMBER   +145

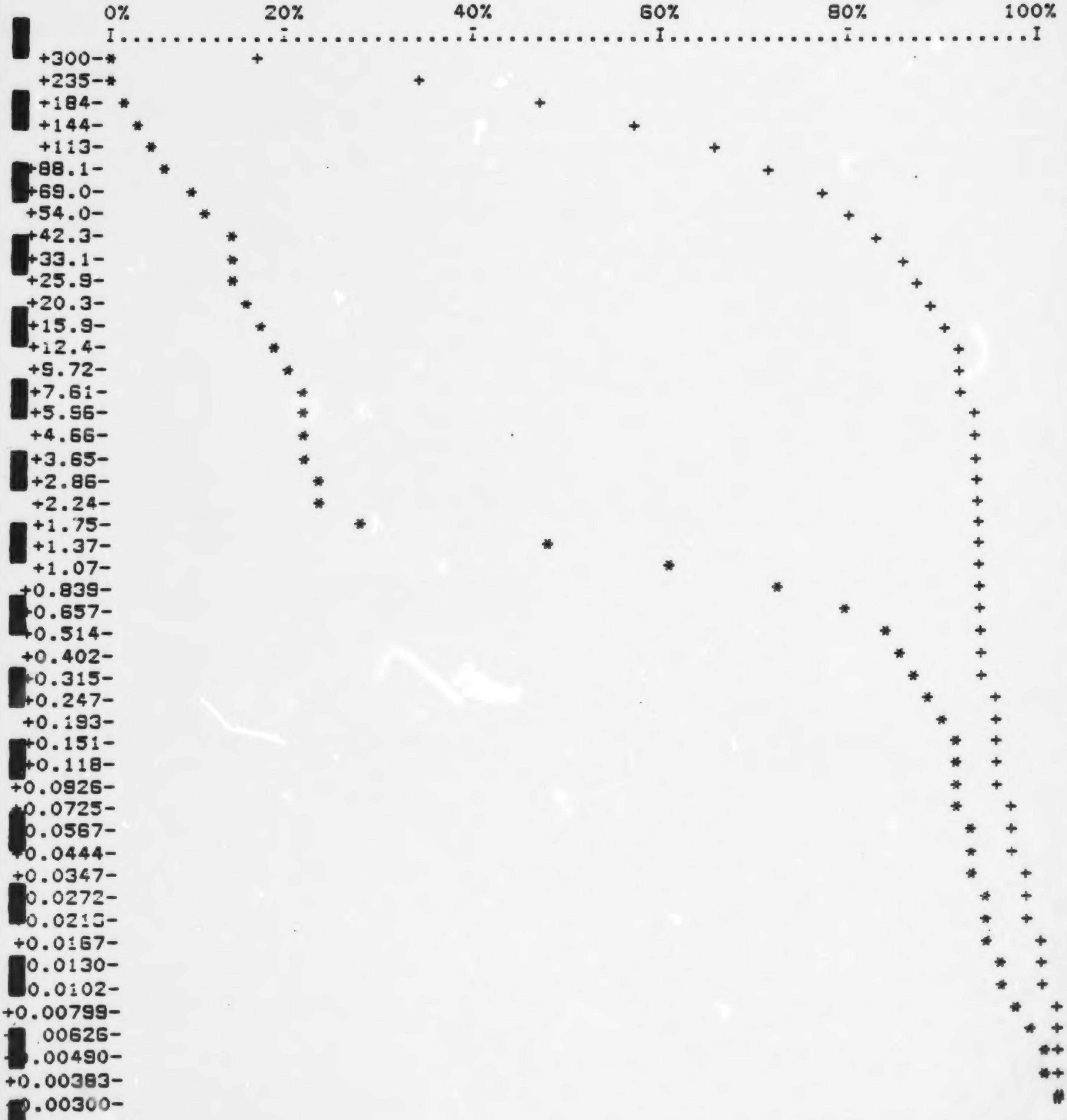
 PRESSURE          PORE          INTRUSION        PORE           MEAN
   PSIA          DIAMETER         VOLUME         SURFACE        DIAMETER              DV
                 MICRO-M           CC/G          SQ-M/G         MICRO-M

 +30031.0        +0.0060          +0.3234        +16.3597       +0.0053            +0.0000
 +20091.3        +0.0090          +0.3211        +15.1428       +0.0075            -0.0023
 +10047.3        +0.0180          +0.3163        +13.7098       +0.0135            -0.0048
   +7543.8       +0.0240          +0.3142        +13.3274       +0.0210            -0.0020
   +5010.4       +0.0361          +0.3121        +13.0406       +0.0300            -0.0022
   +2572.5       +0.0703          +0.3074        +12.6865       +0.0532            -0.0047
   +1004.6       +0.1800          +0.3043        +12.5870       +0.1252            -0.0031
    +750.6       +0.2409          +0.3032        +12.5659       +0.2105            -0.0011
    +498.6       +0.3627          +0.3020        +12.5509       +0.3018            -0.0011
    +248.6       +0.7277          +0.3013        +12.5456       +0.5452            -0.0007
     +99.9       +1.8097          +0.3002        +12.5422       +1.2687            -0.0011
     +74.6       +2.4247          +0.2997        +12.5413       +2.1172            -0.0005
     +50.1       +3.6083          +0.2993        +12.5406       +3.0165            -0.0005
     +25.0       +7.2342          +0.2979        +12.5396       +5.4212            -0.0014
```

N[illegible]RIO RESEARCH FINE PARTICLE LAB
3241
N[illegible] NUMBER +145

LP 9:43:55 12/17/87
HP 10:11:3 12/17/87

CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER
100% = +0.3234



```
NTARIO RESEARCH FINE PARTICLE LAB                        LP 9:43:55 12/17/87
3241                                                     HP 10:11:3 12/17/87
   R NUMBER  +145

             CUMULATIVE SURFACE AREA (M2/G) VS. PORE DIAMETER
                                 100% =    +16.3597

         0%         20%           40%           60%           80%         100%
         I............I............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +88.1-*
   +69.0-*
   +54.0-*
   +42.3-*
   +33.1-*
   +25.9-*
   +20.3-*
   +15.9-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-*
   +1.75-*
   +1.37-*
   +1.07- *
  +0.839- *
  +0.657-  *
  +0.514-  *
  +0.402-  *
  +0.315-   *
  +0.247-   *
  +0.193-   *
  +0.151-   *
  +0.118-    *
 +0.0926-    *
 +0.0725-    *
 +0.0567-    *
 +0.0444-     *
 +0.0347-     *
 +0.0272-      *
 +0.0213-       *
 +0.0167-          *
 +0.0130-             *
 +0.0102-                *
+0.00799-                     *
+0.00626-                           *
+0.00490-                                        *
+0.00383-                                                     *
+0.00300-                                                                    *
```

```
ONTARIO RESEARCH FINE PARTICLE LAB                             LP 9:43:55 12/17/87
3241                                                           HP 10:11:3 12/17/87
PN R NUMBER   +145


                  INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                 100% = +0.522188E-001

         0%           20%           40%           60%           80%          100%
         I.............I.............I.............I.............I.............I
  +300-***
  +235-********
  +184-************
  +144-***************
  +113-******************
 +88.1-*******************
 +69.0-****************
 +54.0-**************
 +42.3-*********
 +33.1-**
 +25.9-*
 +20.3-***
 +15.9-****
 +12.4-**
 +9.72-**
 +7.61-*****
 +5.96-*
 +4.66-*
 +3.65-**
 +2.86-**
 +2.24-*
 +1.75-********************
 +1.37-**********************************************************************
 +1.07-**************************************
+0.839-******************************
+0.657-***************************
+0.514-*****************
+0.402-**********
+0.315-*****
+0.247-****
+0.193-*****
+0.151-***
+0.118-*
+0.0926-**
 0.0725-**
 0.0567-***
+0.0444-***
+0.0347-****
+0.0272-****
+0.0213-***
+0.0167-****
+0.0130-******
+0.0102-********
+0.00799-********
  .00626-*******
  .00490-*******
+0.00383-****
  .00300-*
```

```
NTARIO RESEARCH FINE PARTICLE LAB                                   LP 9:43:55 12/17/87
3241                                                                HP 10:11:3 12/17/87
PN[illegible]R NUMBER   +145

                    INCREMENTAL SURFACE AREA (M2/G) VS. DIAMETER
                                    100% = +0.348723E+001

              0%          20%           40%           60%           80%           100%
              I............I.............I.............I.............I.............I
     +300-*
     +235-*
     +184-*
     +144-*
     +113-*
    +88.1-*
    +69.0-*
    +54.0-*
    +42.3-*
    +33.1-*
    +25.9-*
    +20.3-*
    +15.9-*
    +12.4-*
    +9.72-*
    +7.61-*
    +5.96-*
    +4.66-*
    +3.65-*
    +2.86-*
    +2.24-*
    +1.75-*
    +1.37-***
    +1.07-**
   +0.839-**
   +0.657-**
   +0.514-**
   +0.402-*
   +0.315-*
   +0.247-*
   +0.193-*
   +0.151-*
   +0.118-*
  +0.0926-*
  +0.0725-**
  +0.0567-***
  +0.0444-****
  +0.0347-*****
  +0.0272-******
  +0.0213-*******
  +0.0167-*************
  +0.0130-*************************
  +0.0102-***********************************
 +0.00799-********************************************
 +0.00626-*****************************************************
 +0.00490-**********************************************************************
 +0.00383-**********************************************************
 +0.00300-*
```

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           MICROMERITICS AUTO-PORE 9200 V2.02                         PAGE 1
```

SAMPLE J3242

```
NTARIO RESEARCH FINE PARTICLE LAB                          LP 14:33:56 12/17/87
3 42                                                       HP 14:57:6 12/17/87
   R NUMBER  +147

 LP EQUILIBRATION =    +30.0000 SEC          PNTR CONSTANT =    +27.8200 MICRO-L/PF
 HP EQUILIBRATION =    +30.0000 SEC                  THETA =  +130.0000
    SAMPLE WEIGHT =     +0.8300 G                    GAMMA =  +485.0000 DYNES/CM
      PNTR WEIGHT =    +68.6900 G         INITIAL PRESSURE =     +0.5495 PSIA
 TR+SAMPLE WEIGHT =    +69.5200 G            PORE DIAMETER =  +329.1640 MICRO-M
NTR+SAMPLE+MERCURY =  +139.4800 G          MERCURY DENSITY =    +13.5335 G/CC
      PNTR VOLUME =     +6.6871 CC


I  RUSION (PRESSURIZATION) DATA SUMMARY

      TOTAL INTRUSION VOLUME =      +1.3708 CC/G
             TOTAL PORE AREA =    +52.5431 SQ-M/G
ME IAN PORE DIAMETER  (VOLUME) =    +3.5179 MICROMETERS
MEDIAN PORE DIAMETER  (AREA)   =    +0.0070 MICROMETERS
  AVERAGE PORE DIAMETER (4V/A) =    +0.1044 MICROMETERS
                BULK DENSITY =      +0.5469 G/CC
  APPARENT (SKELETAL) DENSITY =     +2.1846 G/CC

%  CAPILLARY =  +64.5363
```

% POROSITY = 75.0

```
NTARIO RESEARCH FINE PARTICLE LAB                                 LP 14:33:58 12/17/87
3242                                                              HP 14:57:6 12/17/87
N[illegible]R NUMBER   +147

  PRESSURE          PORE          INTRUSION        PORE           MEAN
   PSIA           DIAMETER         VOLUME         SURFACE        DIAMETER              DV
                   MICRO-M          CC/G           SQ-M/G         MICRO-M

      +0.6       +320.6140        +0.0000        +0.0000       +324.8890          +0.0000
      +1.0       +175.0870        +0.0057        +0.0001       +247.8510          +0.0057
      +2.0        +91.7744        +0.0491        +0.0014       +133.4310          +0.0434
      +3.0        +61.2589        +0.0761        +0.0028        +76.5166          +0.0270
      +4.0        +44.9678        +0.0999        +0.0046        +53.1133          +0.0237
      +5.0        +36.1984        +0.1171        +0.0063        +40.5831          +0.0172
      +6.0        +30.1801        +0.1359        +0.0086        +33.1892          +0.0188
      +7.0        +25.9048        +0.1465        +0.0101        +28.0424          +0.0106
      +7.9        +22.8586        +0.1604        +0.0124        +24.3817          +0.0139
      +9.0        +20.1529        +0.1760        +0.0153        +21.5057          +0.0156
     +10.0        +18.1658        +0.1875        +0.0176        +19.1593          +0.0115
     +12.0        +15.0808        +0.2014        +0.0210        +16.6233          +0.0139
     +14.0        +12.9592        +0.2227        +0.0271        +14.0200          +0.0213
     +15.9        +11.3609        +0.2701        +0.0427        +12.1601          +0.0475
     +17.9        +10.0971        +0.2824        +0.0473        +10.7290          +0.0123
     +20.0         +9.0629        +0.2955        +0.0527         +9.5800          +0.0131
     +24.9         +7.2503        +0.3234        +0.0664         +8.1566          +0.0278
     +28.2         +6.4177        +0.3234        +0.0664         +6.8340          +0.0000
     +37.9         +4.7760        +0.3832        +0.1091         +5.5969          +0.0598
     +47.4         +3.8129        +0.6034        +0.3142         +4.2945          +0.2202
     +57.1         +3.1682        +0.7826        +0.5197         +3.4906          +0.1793
     +71.9         +2.5169        +0.8973        +0.6810         +2.8425          +0.1146
     +97.3         +1.8586        +0.9865        +0.8442         +2.1677          +0.0893
    +122.1         +1.4610        +1.0324        +0.9541         +1.6698          +0.0459
    +146.7         +1.2331        +1.0620        +1.0412         +1.3571          +0.0295
    +171.6         +1.0539        +1.0833        +1.1158         +1.1435          +0.0213
    +196.6         +0.9198        +1.0973        +1.1724         +0.9869          +0.0140
    +246.9         +0.7324        +1.1252        +1.3077         +0.8261          +0.0279
    +298.1         +0.6068        +1.1433        +1.4159         +0.6696          +0.0181
    +397.7         +0.4546        +1.1591        +1.5346         +0.5308          +0.0158
    +495.3         +0.3651        +1.1691        +1.6323         +0.4100          +0.0100
    +594.9         +0.3040        +1.1783        +1.7420         +0.3346          +0.0092
    +745.3         +0.2427        +1.1892        +1.9014         +0.2733          +0.0109
    +994.4         +0.1819        +1.2026        +2.1552         +0.2123          +0.0135
   +1247.4         +0.1450        +1.2136        +2.4239         +0.1634          +0.0110
   +1453.5         +0.1211        +1.2221        +2.6786         +0.1330          +0.0085
   +1993.6         +0.0907        +1.2348        +3.1611         +0.1059          +0.0128
   +2982.4         +0.0606        +1.2495        +3.9354         +0.0757          +0.0146
   +4994.0         +0.0362        +1.2676        +5.4314         +0.0484          +0.0181
   +7467.7         +0.0242        +1.2830        +7.4656         +0.0302          +0.0154
   +9956.4         +0.0182        +1.2948        +9.7004         +0.0212          +0.0118
  +19925.8         +0.0091        +1.3241       +18.2953         +0.0136          +0.0293
  +29635.6         +0.0061        +1.3455       +29.6257         +0.0076          +0.0214
  +39954.1         +0.0045        +1.3578       +38.9179         +0.0053          +0.0123
  +49834.1         +0.0036        +1.3668       +47.7108         +0.0041          +0.0090
  +59699.3         +0.0030        +1.3708       +52.5431         +0.0033          +0.0040
  +49769.4         +0.0036        +1.3708       +52.5431         +0.0033          +0.0000
  +40103.1         +0.0045        +1.3708       +52.5431         +0.0041          +0.0000
```

```
ONTARIO RESEARCH FINE PARTICLE LAB                              LP 14:33:58 12/17/87
J3[illegible]42                                                            HP 14:57:6 12/17/87
P[illegible]R NUMBER   +147

 PRESSURE        PORE          INTRUSION        PORE          MEAN
  PSIA         DIAMETER         VOLUME         SURFACE      DIAMETER          DV
               MICRO-M           CC/G          SQ-M/G        MICRO-M

+30059.1       +0.0060         +1.3708        +52.5431      +0.0053        +0.0000
+20074.7       +0.0090         +1.3675        +50.7647      +0.0075        -0.0033
+10045.6       +0.0180         +1.3570        +47.6741      +0.0135        -0.0104
  +7527.2      +0.0240         +1.3509        +46.5114      +0.0210        -0.0061
  +5023.7      +0.0360         +1.3396        +45.0086      +0.0300        -0.0113
  +2497.4      +0.0724         +1.3204        +43.5869      +0.0542        -0.0193
  +1003.0      +0.1803         +1.3033        +43.0466      +0.1264        -0.0171
   +748.0      +0.2418         +1.2980        +42.9463      +0.2110        -0.0053
   +495.1      +0.3653         +1.2902        +42.8435      +0.3035        -0.0078
   +248.0      +0.7294         +1.2791        +42.7622      +0.5473        -0.0111
    +98.0      +1.6448         +1.2616        +42.7077      +1.2871        -0.0175
    +73.0      +2.4776         +1.2541        +42.6940      +2.1612        -0.0074
    +47.9      +3.7765         +1.2451        +42.6824      +3.1271        -0.0091
    +23.1      +7.8351         +1.2319        +42.6733      +5.8058        -0.0132
```

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                    MICROMERITICS AUTO-PORE 9200 V2.02                          PAGE 4

ONTARIO RESEARCH FINE PARTICLE LAB                               LP 14:33:58 12/17/87
J3[illegible]42                                                  HP 14:57:9 12/17/87
F[illegible]R NUMBER  +147


                CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER
                                   100% =      +1.3708

         0%           20%           40%           60%           80%         100%
         I.............I.............I.............I.............I.............I
    +300-*          +
    +235-*                     +
    +184-*                              +
    +144-*                                     +
    +113- *                                          +
   +88.1-  *                                             +
   +69.0-   *                                                +
   +54.0-   *                                                   +
   +42.3-    *                                                    +
   +33.1-     *                                                     +
   +25.9-      *                                                     +
   +20.3-        *                                                    +
   +15.9-         *                                                    +
   +12.4-           *                                                  +
   +9.72-              *                                                +
   +7.61-               *                                               +
   +5.96-                *                                              +
   +4.66-                    *                                          +
   +3.65-                                 *                              +
   +2.86-                                           *                    +
   +2.24-                                                *               +
   +1.75-                                                   *            +
   +1.37-                                                     *           +
   +1.07-                                                       *         +
  +0.839-                                                         *       +
  +0.657-                                                          *      +
  +0.514-                                                           *      +
  +0.402-                                                           *      +
  +0.315-                                                            *     +
  +0.247-                                                             *    +
  +0.193-                                                             *    +
  +0.151-                                                              *    +
  +0.118-                                                              *    +
 +0.0926-                                                               *   +
 +0.0725-                                                                *  +
 +0.0567-                                                                *   +
 +0.0444-                                                                *   +
 +0.0347-                                                                 *  +
 +0.0272-                                                                 *   +
 +0.0213-                                                                  *  +
 +0.0167-                                                                  *  +
 +0.0130-                                                                   *  +
 +0.0102-                                                                   *  +
+0.00799-                                                                    * +
+0.00626-                                                                     *+
+0.00490-                                                                     *+
+0.00383-                                                                      #
+0.00300-                                                                      #
```

```
          MICROMERITICS AUTO-PORE 9200 V2.02

NTARIO RESEARCH FINE PARTICLE LAB                       LP 14:33:58 12/17/87
J3[illegible]2                                          HP 14:57:6 12/17/87
PNTR NUMBER  +147

          CUMULATIVE SURFACE AREA (M2/G) VS. PORE DIAMETER
                          100% =     +52.5431

          0%        20%       40%       60%       80%       100%
          I.........I.........I.........I.........I.........I
     +300-*
     +235-*
     +184-*
     +144-*
     +113-*
    +88.1-*
    +69.0-*
    +54.0-*
    +42.3-*
    +33.1-*
    +25.9-*
    +20.3-*
    +15.9-*
    +12.4-*
    +9.72-*
    +7.61-*
    +5.96-*
    +4.66-*
    +3.65-*
    +2.86-*
    +2.24-*
    +1.75-*
    +1.37-*
    +1.07-*
   +0.839- *
   +0.657- *
   +0.514- *
   +0.402- *
   +0.315- *
   +0.247-  *
   +0.193-  *
   +0.151-  *
   +0.118-   *
  +0.0926-   *
  +0.0725-    *
  +0.0567-    *
  +0.0444-     *
  +0.0347-      *
  +0.0272-       *
  +0.0213-        *
  +0.0167-           *
  +0.0130-               *
  +0.0102-                  *
 +0.00799-                       *
 +0.00626-                              *
 +0.00490-                                      *
 +0.00383-                                               *
 +0.00300-                                                   *
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                               PAGE 6

ONTARIO RESEARCH FINE PARTICLE LAB                                              LP 14:33:58 12/17/87
3242                                                                            HP 14:57:6 12/17/87
PN[illegible]R NUMBER   +147


                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                    100% = +0.209820E+000

          0%           20%           40%           60%           80%         100%
          I.............I.............I.............I.............I.............I
     +300-*
     +235-*
     +184-**
     +144-*******
     +113-***********
    +88.1-**************
    +69.0-**********
    +54.0-*********
    +42.3-*******
    +33.1-******
    +25.5-****
    +20.3-*****
    +15.9-****
    +12.4-**********
    +9.72-****
    +7.61-********
    +5.96-******
    +4.66-**************************
    +3.65-**********************************************************************
    +2.86-*************************************************
    +2.24-***********************************
    +1.75-**************************
    +1.37-*************
    +1.07-*******
   +0.839-*******
   +0.657-*******
   +0.514-******
   +0.402-****
   +0.315-***
   +0.247-****
   +0.193-****
   +0.151-****
   +0.118-***
  +0.0926-****
   0.0725-*****
   0.0567-*****
  +0.0444-******
   0.0347-******
   0.0272-*****
  +0.0213-*****
   0.0167-*****
   0.0130-*******
  +0.0102-*********
 +0.00795-*********
   .00626-*******
  +.00490-*****
 +0.00383-***
   .00300-*
```

```
ONTARIO RESEARCH FINE PARTICLE LAB                            LP 14:33:58 12/17/87
J3[illegible]42                                                       HP 14:57:6 12/17/87
P[illegible]R NUMBER   +147


                  INCREMENTAL SURFACE AREA (M2/G) VS. DIAMETER
                                100% = +0.111550E+002

        0%            20%           40%           60%           80%           100%
         I.............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +88.1-*
   +69.0-*
   +54.0-*
   +42.3-*
   +33.1-*
   +25.9-*
   +20.3-*
   +15.9-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-*
   +3.65-*
   +2.86-*
   +2.24-*
   +1.75-*
   +1.37-*
   +1.07-*
  +0.839-*
  +0.657-*
  +0.514-*
  +0.402-*
  +0.315-*
  +0.247-*
  +0.193-*
  +0.151-**
  +0.118-**
 +0.0926-***
 +0.0725-****
 +0.0567-******
 +0.0444-********
 +0.0347-**********
 +0.0272-************
 +0.0213-*************
 +0.0167-*********************
 +0.0130-*************************************
 +0.0102-*************************************************
 0.00799-************************************************************
  .00626-**********************************************************************
+0.00490-*************************************************************
+0.00383-********************************************************
 0.00300-*
```

SAMPLE J3243

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                      PAGE 1

ONTARIO RESEARCH FINE PARTICLE LAB                              LP 14:33:58 12/17/87
J3243                                                           HP 14:57:6 12/17/87
PNTR NUMBER  +159

   LP EQUILIBRATION =   +30.0000 SEC          PNTR CONSTANT =   +27.8200 MICRO-L/PF
   HP EQUILIBRATION =   +30.0000 SEC                  THETA =  +130.0000
      SAMPLE WEIGHT =    +1.0100 G                    GAMMA =  +485.0000 DYNES/CM
        PNTR WEIGHT =   +68.4900 G         INITIAL PRESSURE =    +0.5495 PSIA
 PNTR+SAMPLE WEIGHT =   +69.5000 G            PORE DIAMETER =  +329.1640 MICRO-M
PNTR+SAMPLE+MERCURY =  +139.6500 G         MERCURY DENSITY =   +13.5335 G/CC
        PNTR VOLUME =    +6.6440 CC


INTRUSION (PRESSURIZATION) DATA SUMMARY

       TOTAL INTRUSION VOLUME =     +0.9838 CC/G
             TOTAL PORE AREA =    +33.4271 SQ-M/G
MEDIAN PORE DIAMETER  (VOLUME) =     +4.4675 MICROMETERS
MEDIAN PORE DIAMETER  (AREA)   =     +0.0059 MICROMETERS
  AVERAGE PORE DIAMETER (4V/A) =     +0.1177 MICROMETERS
                 BULK DENSITY =     +0.6915 G/CC
   APPARENT (SKELETAL) DENSITY =     +2.1632 G/CC

% CAPILLARY =  +56.3622
```

% POROSITY = 68.0

```
                  MICROMERITICS AUTO-PORE 9200 V2.02                           PAGE 2

NTARIO RESEARCH FINE PARTICLE LAB                                   LP 14:33:58 12/17/87
3[illegible]3                                                                  HP 14:57:6 12/17/87
NT[illegible] NUMBER  +159

 PRESSURE       PORE         INTRUSION       PORE          MEAN
   PSIA       DIAMETER        VOLUME        SURFACE      DIAMETER          DV
               MICRO-M         CC/G          SQ-M/G       MICRO-M

     +0.6    +320.6140       +0.0000       +0.0000     +324.8890       +0.0000
     +1.0    +175.0870       +0.0027       +0.0000     +247.8510       +0.0027
     +2.0     +91.7744       +0.0256       +0.0007     +133.4310       +0.0229
     +3.0     +61.2589       +0.0417       +0.0016      +76.5166       +0.0161
     +4.0     +44.9678       +0.0605       +0.0030      +53.1133       +0.0188
     +5.0     +36.1984       +0.0666       +0.0036      +40.5831       +0.0061
     +6.0     +30.1801       +0.0760       +0.0047      +33.1892       +0.0094
     +7.0     +25.9048       +0.0787       +0.0051      +28.0424       +0.0027
     +7.9     +22.8586       +0.0841       +0.0060      +24.3817       +0.0054
     +9.0     +20.1529       +0.0902       +0.0071      +21.5057       +0.0061
    +10.0     +18.1658       +0.0962       +0.0084      +19.1593       +0.0061
    +12.0     +15.0808       +0.1076       +0.0111      +16.6233       +0.0114
    +14.0     +12.9592       +0.1150       +0.0132      +14.0200       +0.0074
    +15.9     +11.3609       +0.1238       +0.0161      +12.1601       +0.0087
    +17.9     +10.0971       +0.1352       +0.0204      +10.7290       +0.0114
    +20.0      +9.0629       +0.1662       +0.0333       +9.5800       +0.0309
    +24.9      +7.2503       +0.1830       +0.0416       +8.1566       +0.0168
    +28.4      +6.3689       +0.1830       +0.0416       +6.8096       +0.0000
    +37.6      +4.8132       +0.4271       +0.2162       +5.5911       +0.2441
    +47.1      +3.8370       +0.6101       +0.3854       +4.3251       +0.1830
    +57.0      +3.1755       +0.6935       +0.4806       +3.5063       +0.0834
    +71.8      +2.5183       +0.7527       +0.5638       +2.8469       +0.0592
    +97.3      +1.8579       +0.7972       +0.6451       +2.1881       +0.0444
   +122.2      +1.4800       +0.8174       +0.6935       +1.6690       +0.0202
   +146.8      +1.2322       +0.8302       +0.7314       +1.3561       +0.0128
   +171.7      +1.0531       +0.8390       +0.7621       +1.1426       +0.0088
   +196.8      +0.9191       +0.8451       +0.7869       +0.9861       +0.0061
   +247.1      +0.7319       +0.8567       +0.8427       +0.8255       +0.0115
   +298.3      +0.6064       +0.8655       +0.8955       +0.6691       +0.0088
   +397.9      +0.4546       +0.8737       +0.9576       +0.5305       +0.0082
   +495.5      +0.3650       +0.8793       +1.0116       +0.4098       +0.0055
   +595.2      +0.3039       +0.8841       +1.0697       +0.3344       +0.0049
   +745.6      +0.2426       +0.8890       +1.1416       +0.2732       +0.0049
   +994.6      +0.1818       +0.8954       +1.2615       +0.2122       +0.0064
  +1247.6      +0.1450       +0.8997       +1.3671       +0.1634       +0.0043
  +1493.8      +0.1211       +0.9026       +1.4551       +0.1330       +0.0029
  +1993.9      +0.0907       +0.9077       +1.6484       +0.1059       +0.0051
  +2992.7      +0.0606       +0.9144       +2.0003       +0.0757       +0.0067
  +4994.3      +0.0362       +0.9232       +2.7298       +0.0484       +0.0088
  +7468.1      +0.0242       +0.9305       +3.6892       +0.0302       +0.0072
  +9956.7      +0.0182       +0.9362       +4.7639       +0.0212       +0.0057
 +19926.1      +0.0091       +0.9528       +9.6543       +0.0136       +0.0167
 +29836.0      +0.0061       +0.9651      +16.1218       +0.0076       +0.0122
 +39954.5      +0.0045       +0.9738      +22.7414       +0.0053       +0.0088
 +49834.5      +0.0036       +0.9798      +28.6479       +0.0041       +0.0060
 +59699.7      +0.0030       +0.9838      +33.4271       +0.0033       +0.0040
 +49789.8      +0.0036       +0.9838      +33.4271       +0.0033       +0.0000
 +40103.4      +0.0045       +0.9838      +33.4271       +0.0041       +0.0000
```

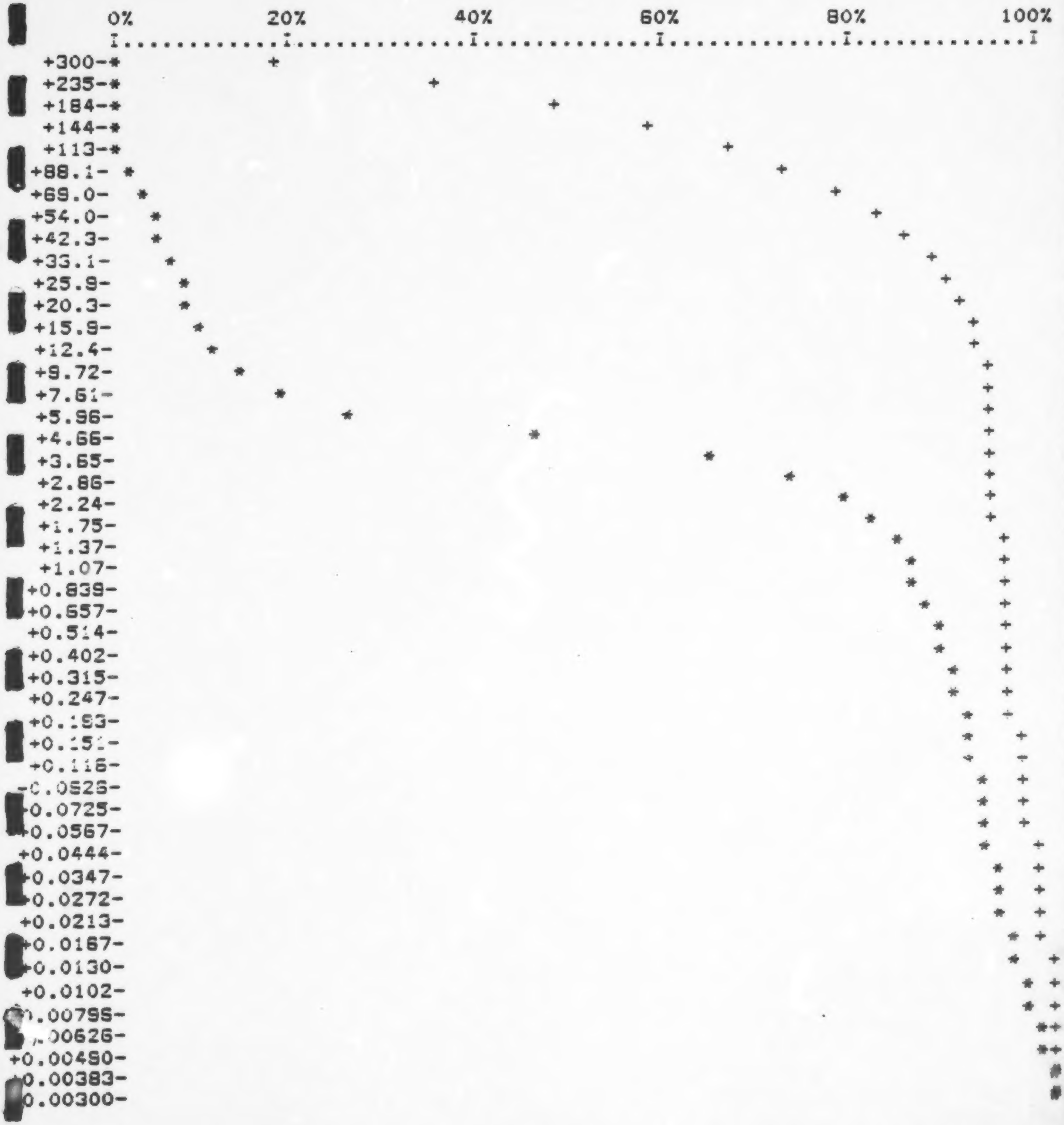
```
NTARIO RESEARCH FINE PARTICLE LAB                              LP 14:33:58 12/17/87
32[illegible]3                                                  HP 14:57:6 12/17/87
N[illegible] NUMBER   +159

 PRESSURE        PORE          INTRUSION        PORE           MEAN
   PSIA        DIAMETER         VOLUME         SURFACE        DIAMETER           DV
               MICRO-M          CC/G           SQ-M/G         MICRO-M

 30059.4       +0.0060         +0.9838        +33.4271        +0.0053         +0.0000
 20075.1       +0.0090         +0.9817        +32.3237        +0.0075         -0.0021
+10046.0       +0.0180         +0.9752        +30.3815        +0.0135         -0.0066
 +7527.6       +0.0240         +0.9708        +29.5540        +0.0210         -0.0043
 +5024.0       +0.0360         +0.9663        +28.9465        +0.0300         -0.0046
 +2497.8       +0.0724         +0.9552        +28.1255        +0.0542         -0.0111
 +1003.3       +0.1803         +0.9465        +27.8518        +0.1263         -0.0086
  +748.4       +0.2417         +0.9435        +27.7948        +0.2110         -0.0030
  +495.4       +0.3651         +0.9411        +27.7635        +0.3034         -0.0024
  +248.3       +0.7285         +0.9380        +27.7409        +0.5468         -0.0031
   +98.3       +1.8398         +0.9337        +27.7274        +1.2841         -0.0043
   +73.3       +2.4689         +0.9323        +27.7248        +2.1543         -0.0014
   +48.1       +3.7577         +0.9309        +27.7231        +3.1133         -0.0014
   +23.3       +7.7625         +0.9295        +27.7221        +5.7601         -0.0014
```

```
ONTARIO RESEARCH FINE PARTICLE LAB                    LP 14:33:58 12/17/87
J3[illegible]43                                       HP 14:57:6 12/17/87
P[illegible]R NUMBER  +159
```

CUMULATIVE PORE VOLUME (CC/G) VS. PORE DIAMETER
100% = +0.9838



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                    MICROMERITICS AUTO-PORE 9200 V2.02                              PAGE 5

ONTARIO RESEARCH FINE PARTICLE LAB                                   LP 14:33:56 12/17/87
J3243                                                                HP 14:57:6 12/17/87
PNTR NUMBER   +159


               CUMULATIVE SURFACE AREA (M2/G) VS. PORE DIAMETER
                                    100% =     +33.4271

        0%          20%          40%          60%          80%          100%
         I............I............I............I............I............I
   +300-*
   +235-*
   +184-*
   +144-*
   +113-*
  +88.1-*
  +69.0-*
  +54.0-*
  +42.3-*
  +33.1-*
  +25.9-*
  +20.3-*
  +15.9-*
  +12.4-*
  +9.72-*
  +7.61-*
  +5.96-*
  +4.66-*
  +3.65-*
  +2.86-*
  +2.24-*
  +1.75-*
  +1.37-*
  +1.07- *
 +0.839- *
 +0.657- *
 +0.514- *
 +0.402- *
 +0.315- *
 +0.247- *
 +0.193-  *
 +0.151-  *
 +0.118-  *
+0.0926-  *
 0.0725-   *
 0.0567-   *
+0.0444-    *
 0.0347-     *
 0.0272-      *
+0.0213-        *
 0.0167-           *
 0.0130-              *
+0.0102-                 *
+0.00799-                      *
 .00626-                              *
+0.00490-                                         *
+0.00383-                                                     *
 0.00300-                                                                 *
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                         PAGE 8

ONTARIO RESEARCH FINE PARTICLE LAB                         LP 14:33:58 12/17/87
3 43                                                       HP 14:57:6 12/17/87
PN R NUMBER   +159


                    INCREMENTAL VOLUME (CC/G) VS. PORE DIAMETER
                                 100% = +0.234659E+000

        0%           20%            40%            60%            80%           100%
        I..............I..............I..............I..............I..............I
  +300-*
  +235-*
  +184-*
  +144-***
  +113-*****
 +88.1-*******
 +69.0-*****
 +54.0-*****
 +42.3-****
 +33.1-**
 +25.9-*
 +20.3-**
 +15.9-***
 +12.4-**
 +9.72-******
 +7.61-******
 +5.96-*******************
 +4.66-**********************************************************************
 +3.65-**********************************************
 +2.86-*********************
 +2.24-****************
 +1.75-***********
 +1.37-*****
 +1.07-***
 0.839-***
 0.657-***
+0.514-***
 0.402-**
 0.315-*
+0.247-*
 0.193-**
 0.151-*
+0.118-*
 0.0926-*
 0.0725-**
 0.0567-**
+0.0444-**
 0.0347-***
 0.0272-**
+0.0213-**
 0.0167-**
 0.0130-****
+0.0102-*****
 .00799-****
 .00626-****
+0.00490-***
 .00383-**
 .00300-*
```

```
                    MICROMERITICS AUTO-PORE 9200 V2.02                       PAGE 7

ONTARIO RESEARCH FINE PARTICLE LAB                               LP 14:33:58 12/17/87
J3243                                                            HP 14:57:6 12/17/87
PN R NUMBER   +159


                 INCREMENTAL SURFACE AREA (M2/G) VS. DIAMETER
                                100% = +0.658298E+001

         0%           20%           40%           60%           80%          100%
         I.............I.............I.............I.............I.............I
    +300-*
    +235-*
    +184-*
    +144-*
    +113-*
   +88.1-*
   +69.0-*
   +54.0-*
   +42.3-*
   +33.1-*
   +25.9-*
   +20.3-*
   +15.9-*
   +12.4-*
   +9.72-*
   +7.61-*
   +5.96-*
   +4.66-**
   +3.65-**
   +2.86-*
   +2.24-*
   +1.75-*
   +1.37-*
   +1.07-*
  +0.839-*
  +0.657-*
  +0.514-*
  +0.402-*
  +0.315-*
  +0.247-*
  +0.193-*
  +0.151-*
  +0.118-*
 +0.0926-**
  0.0725-***
  0.0567-****
 +0.0444-******
  0.0347-********
  0.0272-**********
 +0.0213-***********
  0.0167-******************
  0.0130-**********************************
 +0.0102-***********************************************
+0.00799-**********************************************************
  .00626-********************************************************************
  .00490-**********************************************************************
+0.00383-*****************************************************************
  .00300-*
```

APPENDIX II: Image Analysis Assessment of Particle Size

RESEA[illegible]

2395 Speakman Drive
Mississauga, Ontario [illegible]
(416) 822-4111 or 1-800-268-[illegible]
Telex 06-982311 Fax [illegible]

Craig Booth
Dept. PPCTR

January 13, 1988

REPORT NUMBER IA 202-88-1

IDENTIFICATION W.O.# 29726

SPECIFICATIONS OF ORDER Particle Size Analysis of Five Brown Powders

---

INTRODUCTION

Five brown powders were received for particle size analysis by volume percent. The samples were identified as follows:

J#3239 BHA Float Tailing
J#3240 ESP Float Tailing
J#3241 3:1 ESP:BHA Float Tailing
J#3242 NaOH Leach Tailing
J#3243 Na_2CO_3 Leach Tailing

[illegible] ONTARIO RESEARCH FOUNDATION STIPULATE THAT THIS DOCUMENT IS SUBJECT TO THE FOLLOWING TERMS AND CON[illegible]
[illegible] ANY PROPOSAL CONTAINED HEREIN WAS PREPARED FOR THE CONSIDERATION OF THE ADDRESSEE ONLY. ITS CONTENTS [illegible]
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2. ANY TESTING, INSPECTION OR INVESTIGATION PERFORMED BY US WILL BE CONDUCTED IN ACCORDANCE WITH NORMAL [illegible]
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3. ANY REPORT, PROPOSAL OR QUOTATION PREPARED BY US REFERS ONLY TO THE PARTICULAR MATERIAL, INSTRUMENT [illegible]
REPRESENTATION IS MADE THAT SIMILAR ARTICLES WILL BE OF LIKE QUALITY.
4. NO REPORT ISSUED BY US SHALL BE PUBLISHED IN WHOLE OR IN PART WITHOUT OUR PRIOR WRITTEN CONSENT.
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6. WE RESERVE THE RIGHT NOT TO COMMENCE AND/OR CONTINUE ANY WORK UNTIL PAYMENT ARRANGEMENTS SATISFACTOR[illegible]

METHOD

A small portion of each sample was mixed with a hydrocarbon-based dispersing solution in the ultrasonic bath for one minute in order to break up any loosely bound agglomerates. A few drops of each mixture were placed on a microscope slide and a coverslip was placed on top. The samples were viewed in transmitted illumination on the optical microscope at a magnification of 125X. Images of the particles were transferred by video camera to the television monitor of the LeMont OASYS Optical Analysis System which automatically calculated the equivalent circular diameters of the particles. The resulting frequency percent distributions were converted to volume percent distributions by assuming spherical particle shape. The smallest particle which could be sized by this method was 1.3 micrometres.

Representative photomicrographs of the samples were taken at 315X and 500X.

RESULTS

The size distribution data based on diameter size by volume percent are given in Tables I to V and plotted as histograms in Figures 1 to 5. A summary of the data is given in the table below.

Representative photomicrographs of the samples are given in Figures 6 to 15.

	Particle Size (Micrometres)		
Sample	Average	RMS Deviation	Maximum Analysed
J#3239	21	18	90
J#3240	18	12	45
J#3241	11	7	34
J#3242	14	10	39
J#3243	13	9	36

A.J. Terry
Sr. Technologist

K.L. Yan, Ph.D.
Section Manager

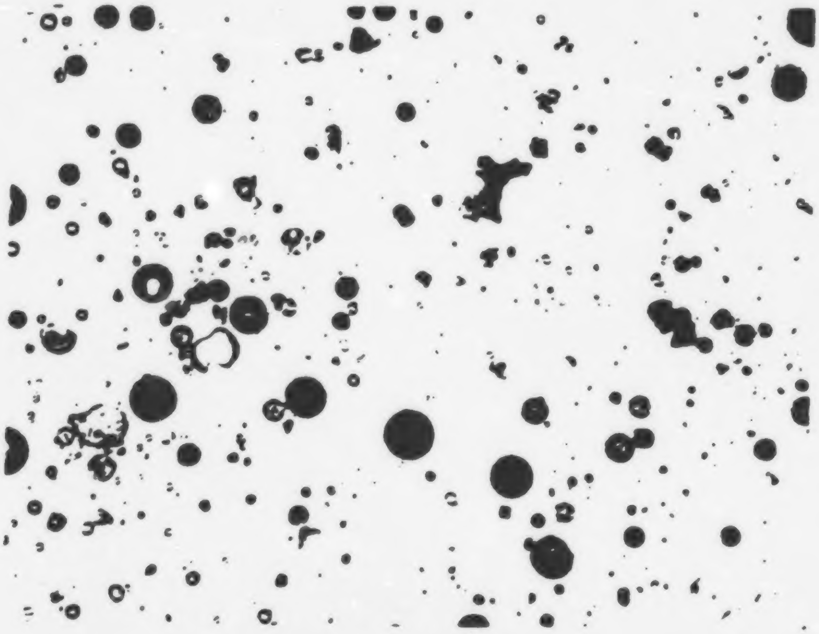

FIGURE 6 J#3239 315X

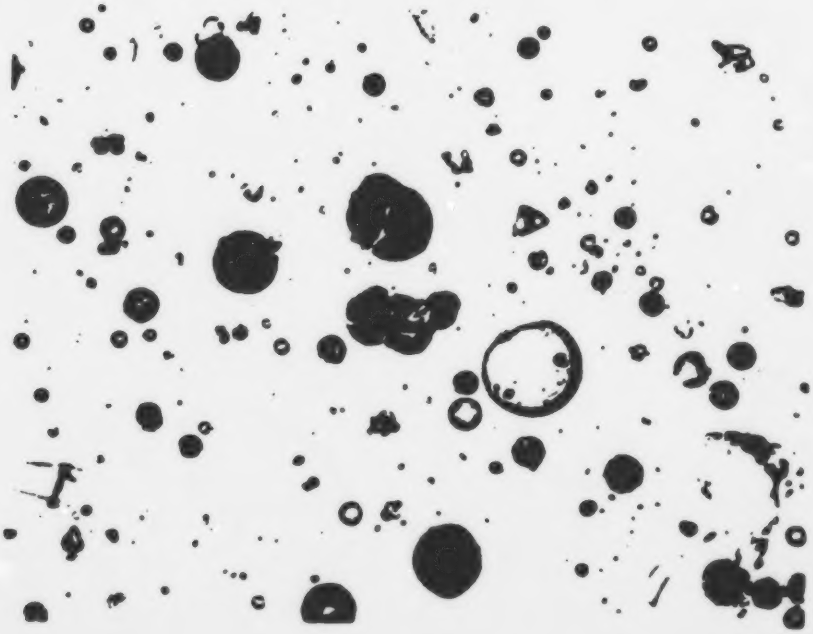

FIGURE 7 J#3239 500X

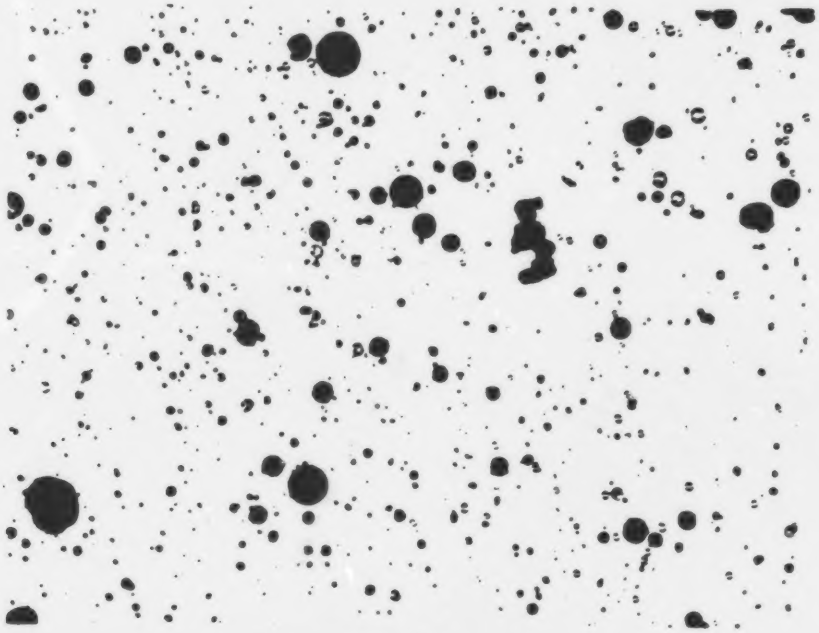

FIGURE 8 J#3240 315X

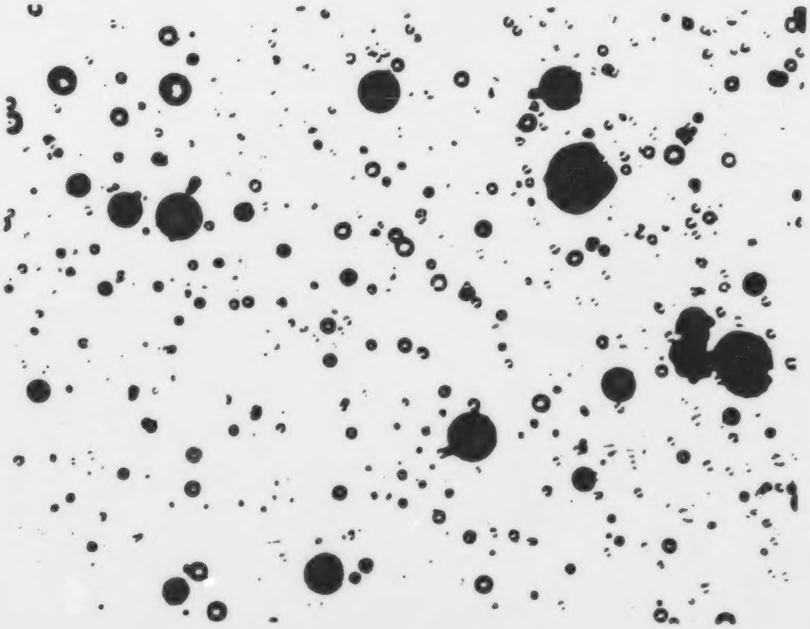

FIGURE 9 J#3240 500X

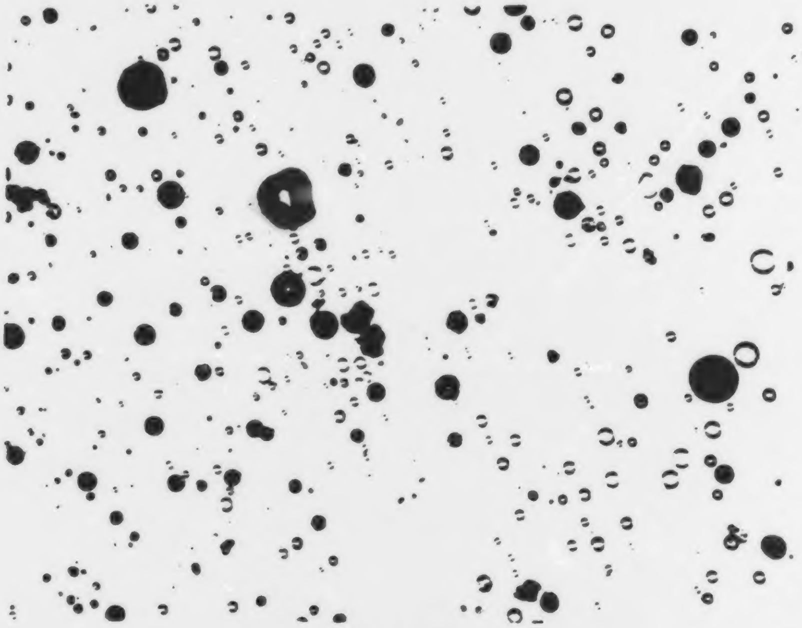

FIGURE 10 J#3241 315X

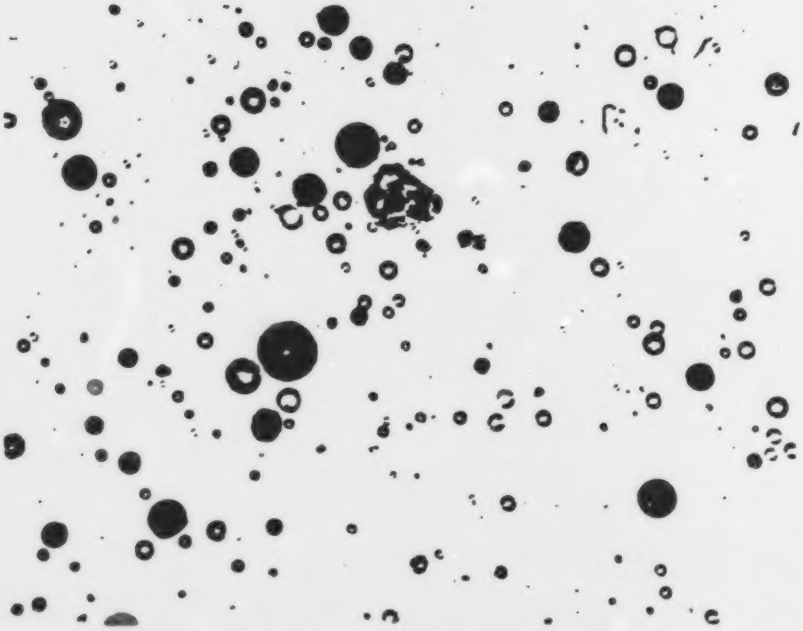

FIGURE 11 J#3241 500X

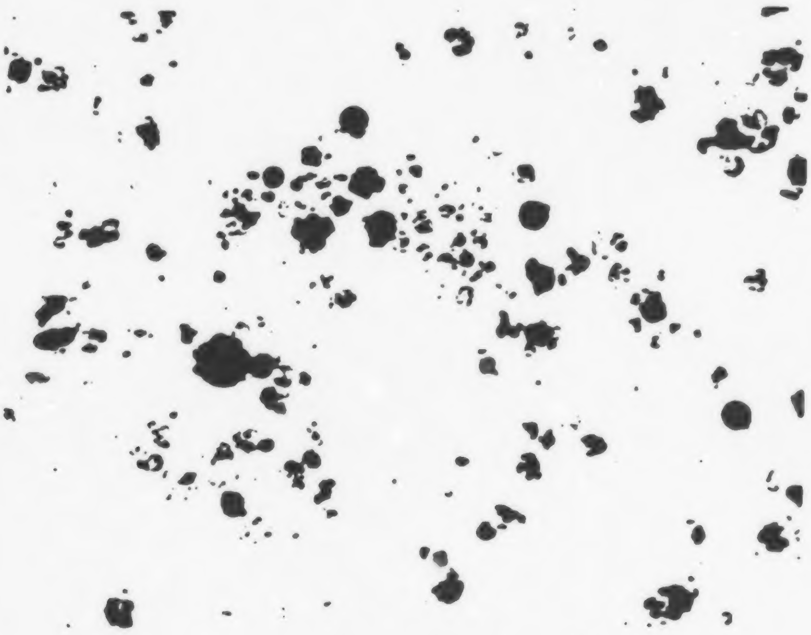

FIGURE 12 J#3242 315X

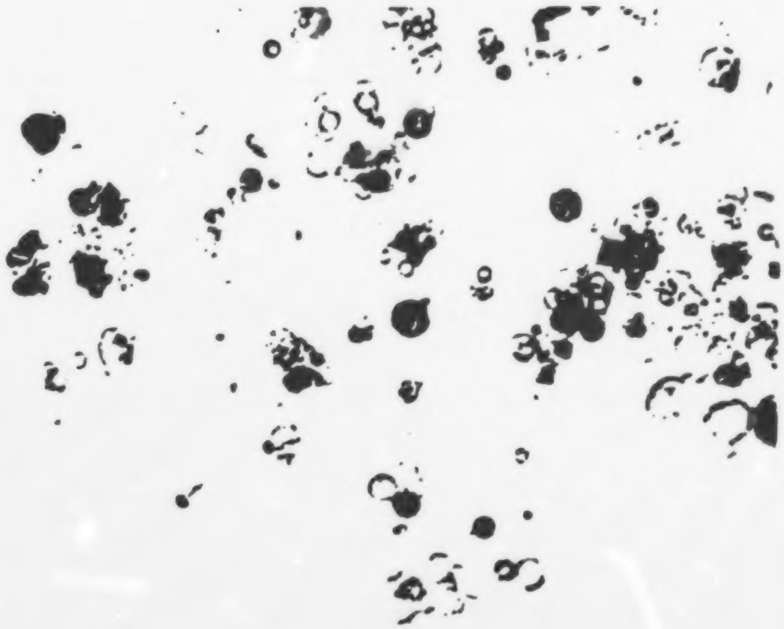

FIGURE 13 J#3242 500X

TABLE I

J#3239 BHA FLOAT TAILING

DIAMETER CLASS INTERVAL (MICROMETRES)	FREQUENCY	VOLUME PERCENT	CUMULATIVE VOLUME PERCENT
1.3 - 2	1338	0.1	0.1
2 - 4	2138	1.4	1.5
4 - 6	1357	4.1	5.6
6 - 8	731	6.0	11.7
8 - 10	361	6.3	18.0
10 - 12	210	6.7	24.7
12 - 14	145	7.7	32.4
14 - 16	101	8.2	40.6
16 - 18	55	6.5	47.1
18 - 20	42	6.9	54.0
20 - 22	21	4.7	58.7
22 - 24	17	5.0	63.7
24 - 26	9	3.4	67.1
26 - 28	10	4.7	71.8
28 - 30	7	4.1	75.9
30 - 32	3	2.2	78.1
32 - 34	1	0.9	78.9
34 - 36	0	0.0	78.9
36 - 38	1	1.2	80.2
38 - 40	0	0.0	80.2
40 - 90	3	19.8	100.0
	6550		

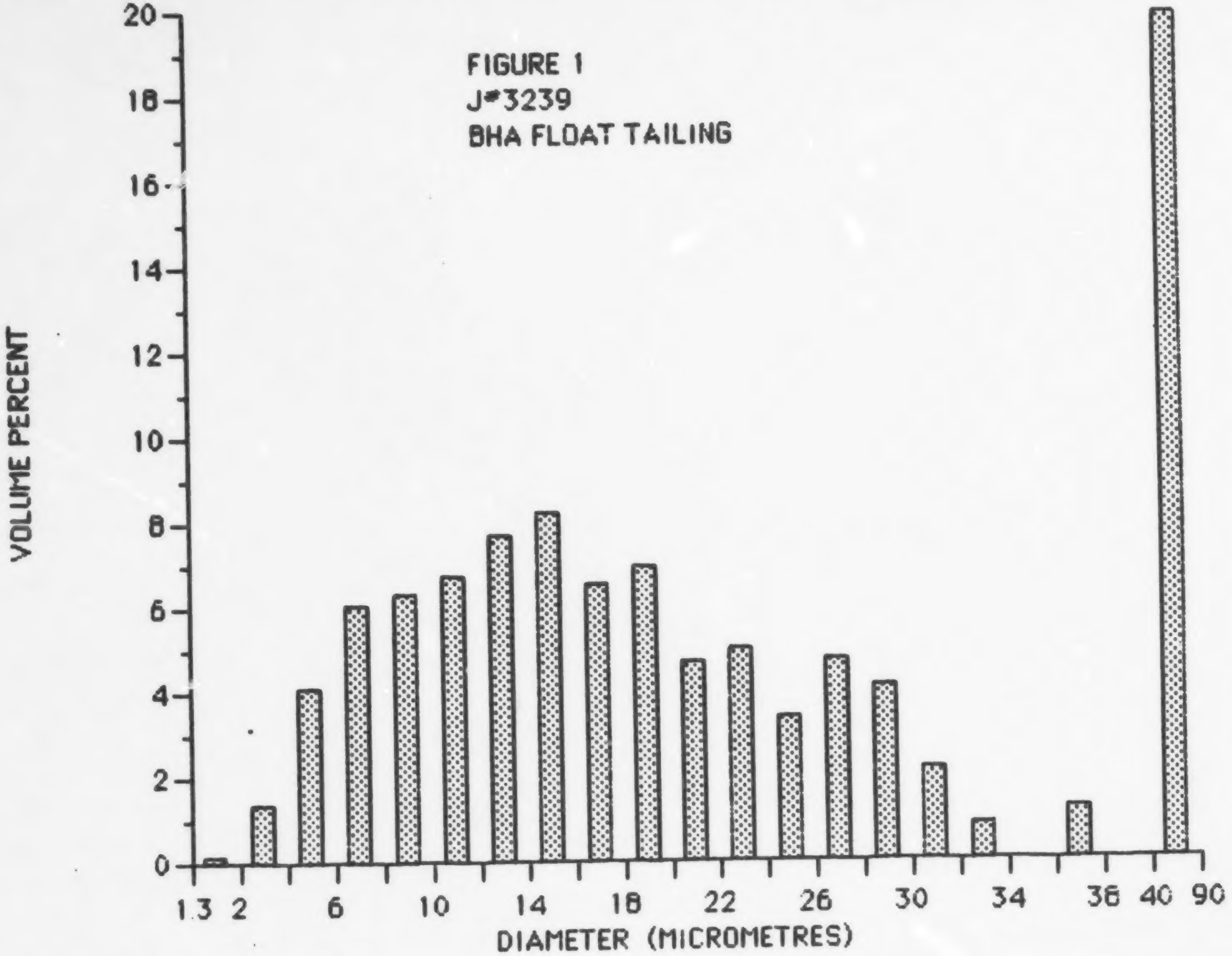

FIGURE 1
J#3239
BHA FLOAT TAILING

TABLE II

J*3240 ESP FLOAT TAILING

DIAMETER CLASS INTERVAL (MICROMETRES)	FREQUENCY	VOLUME PERCENT	CUMULATIVE VOLUME PERCENT
1.3 - 2	1645	0.9	0.9
2 - 4	2735	8.6	9.5
4 - 6	1108	16.2	25.7
6 - 8	262	10.5	36.2
8 - 10	102	8.7	44.9
10 - 12	54	8.4	53.3
12 - 14	21	5.4	58.7
14 - 16	11	4.3	63.0
16 - 18	9	5.2	68.2
18 - 20	10	8.0	76.2
20 - 22	1	1.1	77.3
22 - 24	4	5.7	83.0
24 - 26	1	1.8	84.8
26 - 28	2	4.6	89.4
28 - 45	1	10.6	100.0
	5966		

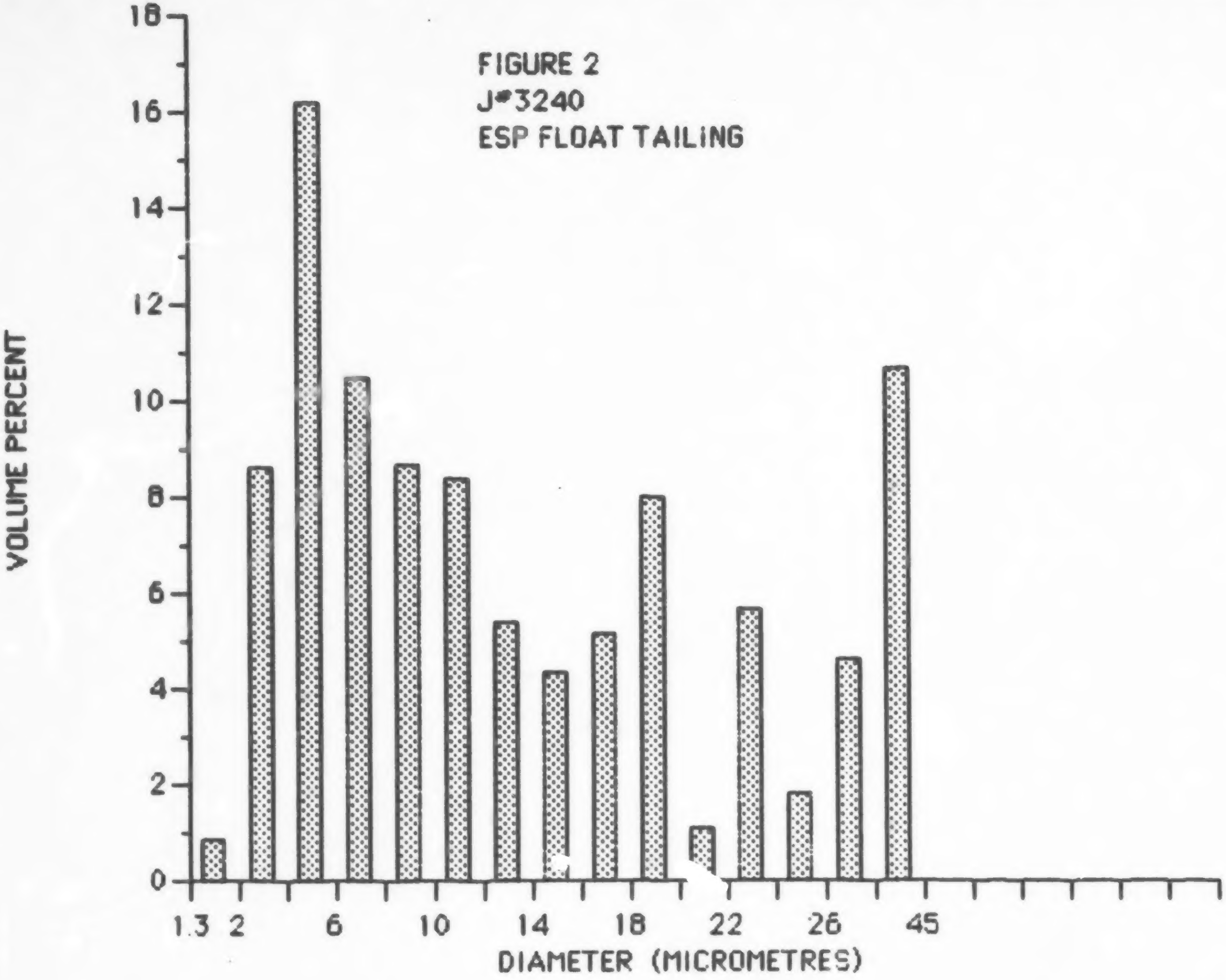

FIGURE 2
J#3240
ESP FLOAT TAILING

TABLE III

J#3241 ESP:BHA FLOAT TAILING

DIAMETER CLASS INTERVAL (MICROMETRES)	FREQUENCY	VOLUME PERCENT	CUMULATIVE VOLUME PERCENT
1.3 - 2	1128	0.4	0.4
2 - 4	1895	4.1	4.5
4 - 6	1326	13.2	17.6
6 - 8	535	14.6	32.2
8 - 10	228	13.2	45.4
10 - 12	96	10.2	55.6
12 - 14	62	10.8	66.4
14 - 16	26	7.0	73.4
16 - 18	23	9.0	82.4
18 - 20	5	2.7	85.1
20 - 22	4	2.9	88.0
22 - 24	3	2.9	90.9
24 - 26	1	1.2	92.2
26 - 28	3	4.7	96.9
28 - 34	1	3.1	100.0
	5336		

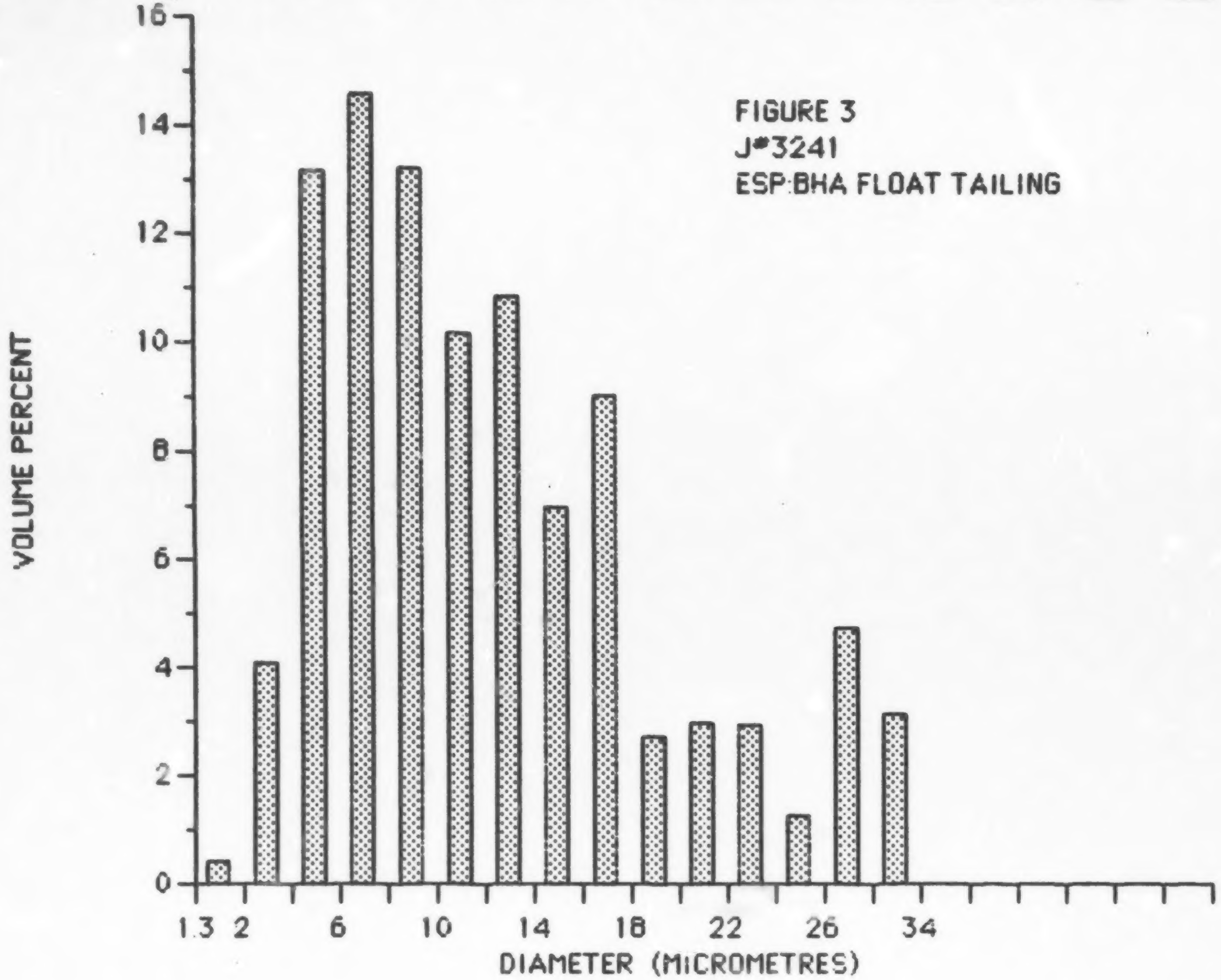

FIGURE 3
J#3241
ESP:BHA FLOAT TAILING

TABLE IV

J*3242 NAOH LEACH TAILING

DIAMETER CLASS INTERVAL (MICROMETRES)	FREQUENCY	VOLUME PERCENT	CUMULATIVE VOLUME PERCENT
1.3 - 2	505	0.1	0.1
2 - 4	941	1.6	1.7
4 - 6	660	5.1	6.7
6 - 8	392	8.2	15.0
8 - 10	234	10.5	25.4
10 - 12	137	11.2	36.6
12 - 14	74	10.0	46.6
14 - 16	45	9.3	55.9
16 - 18	26	7.8	63.7
18 - 20	14	5.9	69.6
20 - 22	8	4.5	74.1
22 - 24	8	6.0	80.1
24 - 26	4	3.8	83.9
26 - 28	2	2.4	86.3
28 - 30	1	1.5	87.8
30 - 32	2	3.7	91.5
32 - 34	1	2.2	93.7
34 - 36	1	2.6	96.3
36 - 39	1	3.6	100.0
	3056		

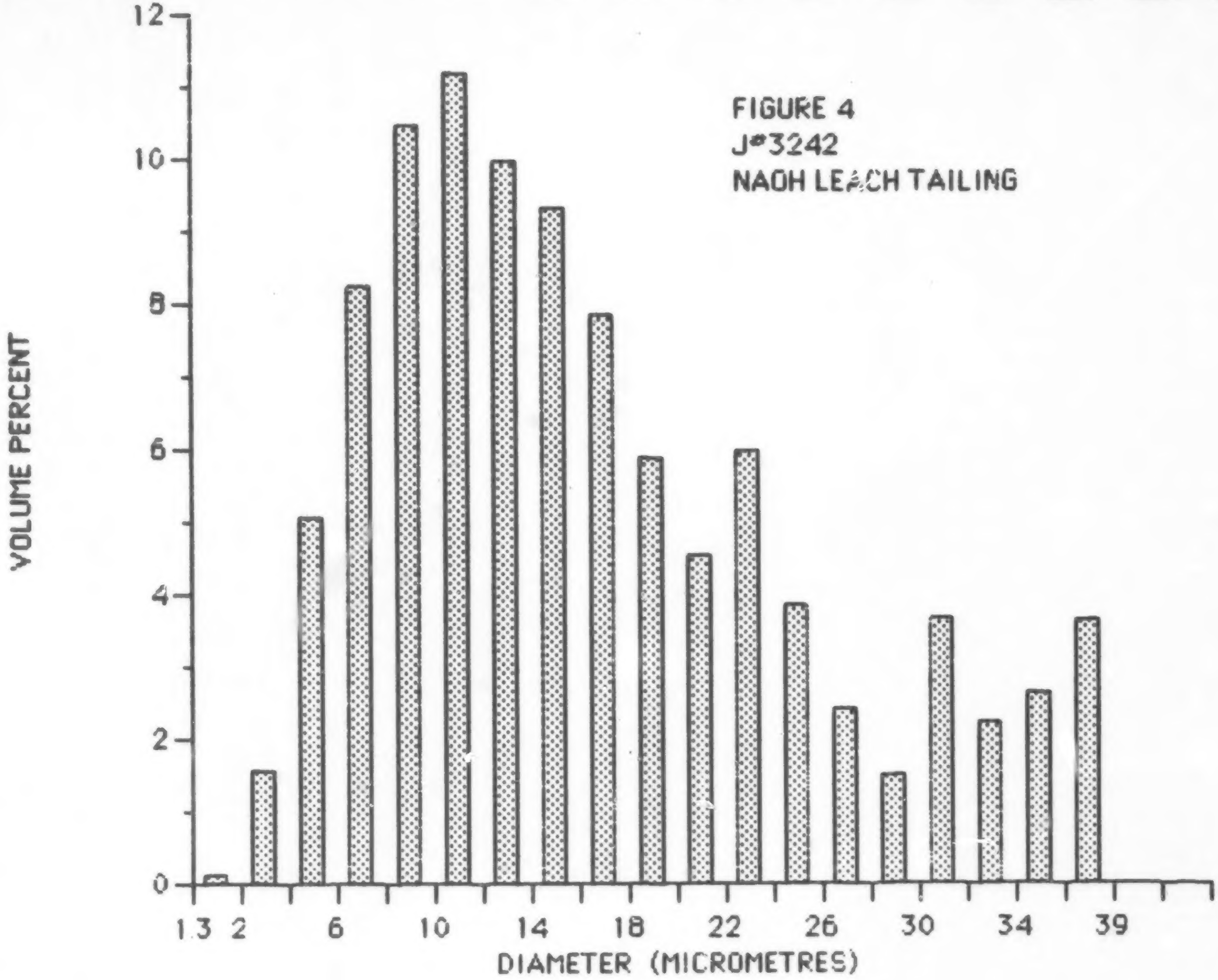

FIGURE 4
J#3242
NAOH LEACH TAILING

TABLE V

J#3243 NA2CO3 LEACH TAILING

DIAMETER CLASS INTERVAL (MICROMETRES)	FREQUENCY	VOLUME PERCENT	CUMULATIVE VOLUME PERCENT
1.3 - 2	301	0.1	0.1
2 - 4	656	1.2	1.3
4 - 6	685	5.9	7.2
6 - 8	369	8.7	15.9
8 - 10	169	8.5	24.3
10 - 12	129	11.8	36.1
12 - 14	89	13.4	49.6
14 - 16	57	13.2	62.8
16 - 18	31	10.5	73.2
18 - 20	11	5.2	78.4
20 - 22	11	7.0	85.4
22 - 24	0	0.0	85.4
24 - 26	5	5.4	90.8
26 - 28	2	2.7	93.5
28 - 30	2	3.3	96.8
30 - 36	1	3.2	100.0
	2518		

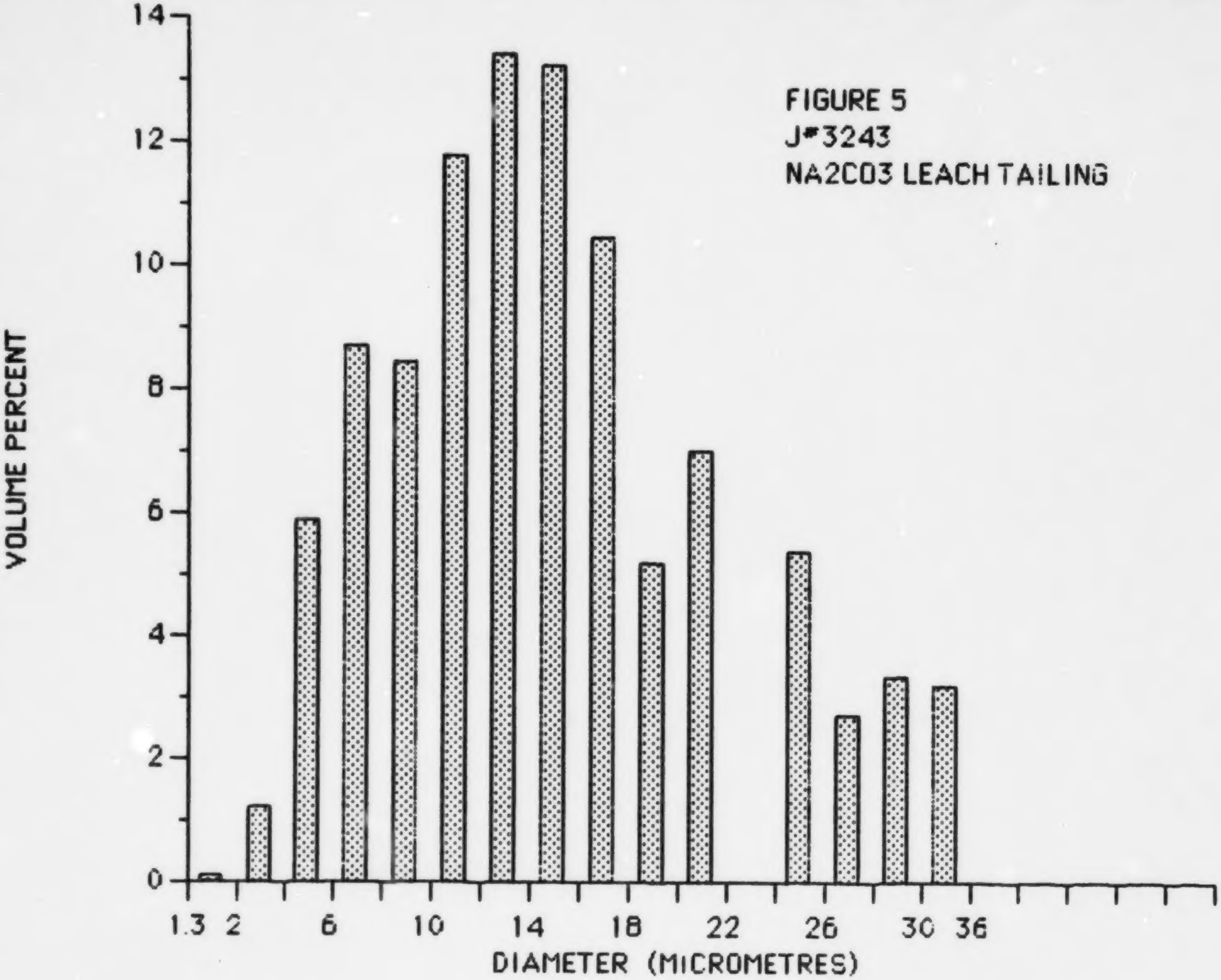

FIGURE 5
J#3243
NA2CO3 LEACH TAILING

1AT

Fabrication of FCC Catalysts from Suncor Flyash Leach Residue

Progress Report #4

for

Carbovan Inc.
2200 Argentia Road
Mississauga, Ontario
L5N 2K7

Attn: Mr. Nairn McQueen

V. I. Lakshmanan
I. A. Todd
G. M. Freeman
Mineral Resources

ORF Account No. 41-10874
DSS Contract Serial No. 23440-7-9124/01-SQ

February 24, 1988

Fabrication of FCC Catalysts from Suncor Flyash Leach Residue For Carbovan Inc.

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1. INTRODUCTION

The present report details the status of Tasks 1-4 in the project.

Task 1 Summary

This task is complete as reported in Progress Report No. 1.

Task 2 Specification Analysis/Literature Search

As reported in Progress Report No. 3 as many specifications as are publicly available have been collated.

The literature search is complete and a report is in preparation addressing not only the present specifications of zeolites in the major areas of application but also the future trends for zeolite use. Preliminary data suggests that zeolites in the synthetic form with highly specialized characteristics will be more easily marketable than material whose function is already adequately covered by present available zeolites.

Task 3 Evaluation of Physical and Chemical Properties

Further data is available on the bulk samples of leached tailings including particle size, and porosimetry by N_2BET method including the measured pore size. (Appendix 1). Caustic leach tailings show an average physical pore size of 120A compared to 83A for caustic/soda ash leach tails.

Further chemical analysis on these samples is given in Appendix II.

Task 4 Evaluation of Unmodified Leach Residue

Material tests for zeolite application in the four major markets, i.e. catalyst, microsieves, fillers, detergents, have yet to be completed though results are expected imminently and will hopefully be available for the next progress report.

2. TASK COMPLETION SUMMARY

Task 1	Summary	Complete
Task 2	Specification Analysis	95% Complete
Task 3	Evaluate Physical and Chemical Properties	95% Complete
Task 4	Evaluate Unmodified Leach Residue	75% Complete

The project is presently on budget to complete Tasks 1-4.

V. I. Lakshmanan
Project Manager
Mineral Resources

Freeman
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I. A. Todd
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APPENDIX I: Analyses of "ES1" and "ES2"

I. Todd
Mineral Resources
February 17, 1988

REPORT NUMBER FPL 66-50005-88-14

IDENTIFICATION W.O.# 30253

SPECIFICATIONS OF ORDER
ANALYSIS ES1 CAUSTIC/SODA ASH TAILS
ANALYSIS ES2 CAUSTIC TAILS

---

1. INTRODUCTION

Two samples labelled, "ES1" and "ES2" were received for various analyses.

2. METHOD

2.1 Surface Area Pore Volume

The surface area/pore volume was determined using the Micromeritics ASAP 2400. The adsorbate gas used was nitrogen. The work was performed by Micromeritic's Materials Analysis Laboratory Services in Georgia.

2.2 Particle Size Distribution

2.2.1 Coulter Counter

A representative portion of the sample was suspended in approximately 20 ml of Isoton II (a particle-free 0.8% NaCl aqueous electrolyte). The sample was then subjected to a low-power ultrasonic bath for thirty seconds to aid in de-agglomerating any loosely bound aggregates. A portion of the sample was then extracted by pipette for analysis on the Coulter Counter which is based on the electrical zone sensing method.

2.2.2 Image Analysis

A small portion of each sample was mixed with a hydrocarbon-based dispersing solution in the ultrasonic bath for a minute in order to break up any loosely bound agglomerates. A few drops of each mixture were pipetted onto microscope slides and coverslips were set on top. The samples were viewed in transmitted illumination on the optical microscope at a magnification of 125X. Images of the particles were transferred via the video camera to the television monitor of the LeMont OASYS Optical Analysis System. Equivalent circular diameters were automatically calculated by the image analyser. The resulting frequency percent distribution was converted to volume percent distribution by assuming spherical particles. The smallest particle which could be analysed at this magnification was 1.7 micrometers.

2.3 Density

The wet density was measured in duplicate using 25 ml pycnometers with ethanol as the dispersant.

The dry density (bulk density) was measured using 100 ml graduated cylinders. The volumes were measured before and after vibration with a vibrating table.

3. RESULTS

The densities, particle size and surface area/pore volume are summarized in Table 1. Appendix 1 gives the data and graphical representations.

Bradley Smith

B. Smith
Project Technician

K. L. Yan, Ph.D
Section Manager

PHYSICAL CHARACTERISATION ~~OF~~ LEACH TAILS.

TABLE 1

~~SUMMARY OF VARIOUS TESTS FOR SAMPLES ES1 and ES2~~

	Sample I.D. ~~ES1~~ CAUSTIC/SODA ASH TAILS	 ~~ES2~~ CAUSTIC TAILS.
DENSITIES (g/cc)		
Wet	2.48	2.60
Bulk	0.67	0.57
Tapped	0.79	0.59
OPTICAL ANALYSIS		
Average Size (μm)	15	15
Geometric Mean (Standard Deviation)	1.9	1.9
COULTER ANALYSIS		
Median (μm)	11.7	10.1
* SURFACE AREA (m^2/g)	38.2	59.3
* PORE VOLUME (cc/g)	0.08	0.18
* AVERAGE PORE DIAMETER (Å)	83.16	120.6

~~ES1 = CAUSTIC/SODA ASH LEACH TAILS~~

~~ES2 = CAUSTIC LEACH TAILS~~

Oil adsorption**	48.4	57.7
pH***	10.1	10.3

* From N_2 BET measurements.

** ASTM D281

*** ASTM D3100

APPENDIX 1

Data and Graphical outputs of the various analyses for Samples ES1 and ES2

TABLE I

SIZE DISTRIBUTION FOR SAMPLE ES2 (CAUSTIC LEACH TAILS)

DIAMETER CLASS INTERVAL (MICROMETRES)	FREQUENCY	VOLUME PERCENT	CUMULATIVE VOLUME PERCENT
1.7 - 2	789	0.1	100.0
2 - 4	2545	1.0	99.9
4 - 6	2784	4.8	99.0
6 - 8	1234	5.9	94.1
8 - 10	613	6.2	88.2
10 - 12	430	8.0	82.0
12 - 14	419	12.8	74.0
14 - 16	264	12.4	61.2
16 - 18	158	10.8	48.8
18 - 20	110	10.5	38.0
20 - 22	64	8.3	27.5
22 - 24	30	5.1	19.2
24 - 26	14	3.0	14.1
26 - 28	13	3.6	11.1
28 - 30	8	2.7	7.5
30 - 32	4	1.7	4.8
32 - 34	2	1.0	3.2
34 - 36	1	0.6	2.2
36 - 38	1	0.7	1.6
38 - 41	1	0.9	0.9
	9484		

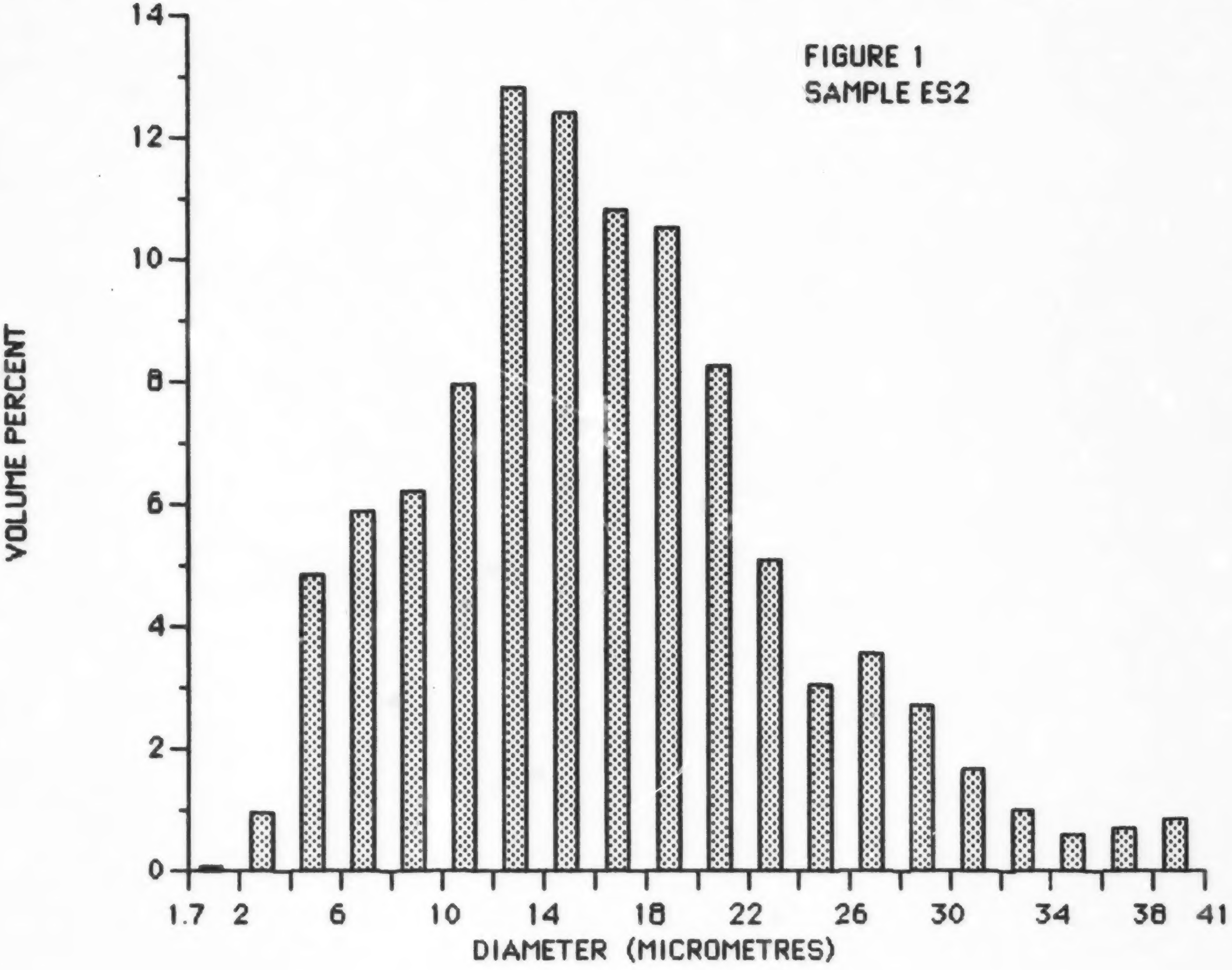


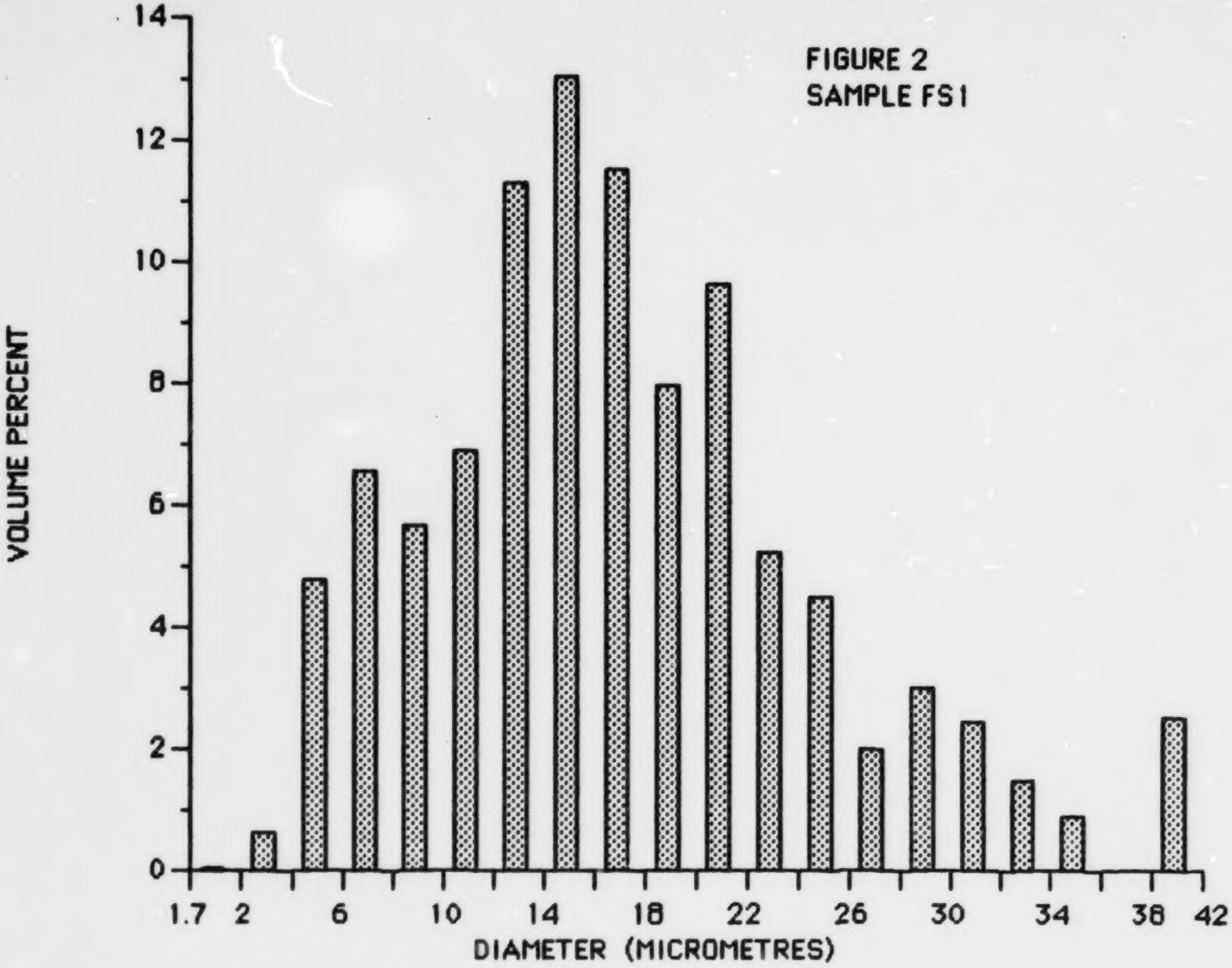
FIGURE 1
SAMPLE ES2

TABLE II

SIZE DISTRIBUTION FOR SAMPLE FS1 (CAUSTIC/SODA ASH TAILS)

DIAMETER CLASS INTERVAL (MICROMETRES)	FREQUENCY	VOLUME PERCENT	CUMULATIVE VOLUME PERCENT
1.7 - 2	378	0.0	100.0
2 - 4	1117	0.6	100.0
4 - 6	1875	4.8	99.3
6 - 8	935	6.5	94.6
8 - 10	380	5.7	88.0
10 - 12	254	6.9	82.3
12 - 14	252	11.3	75.4
14 - 16	189	13.0	64.1
16 - 18	115	11.5	51.1
18 - 20	57	8.0	39.6
20 - 22	51	9.6	31.6
22 - 24	21	5.2	22.0
24 - 26	14	4.5	16.8
26 - 28	5	2.0	12.3
28 - 30	6	3.0	10.3
30 - 32	4	2.4	7.3
32 - 34	2	1.5	4.9
34 - 36	1	0.9	3.4
36 - 38	0	0.0	2.5
38 - 42	2	2.5	2.5
	5658		

FIGURE 2
SAMPLE FS1

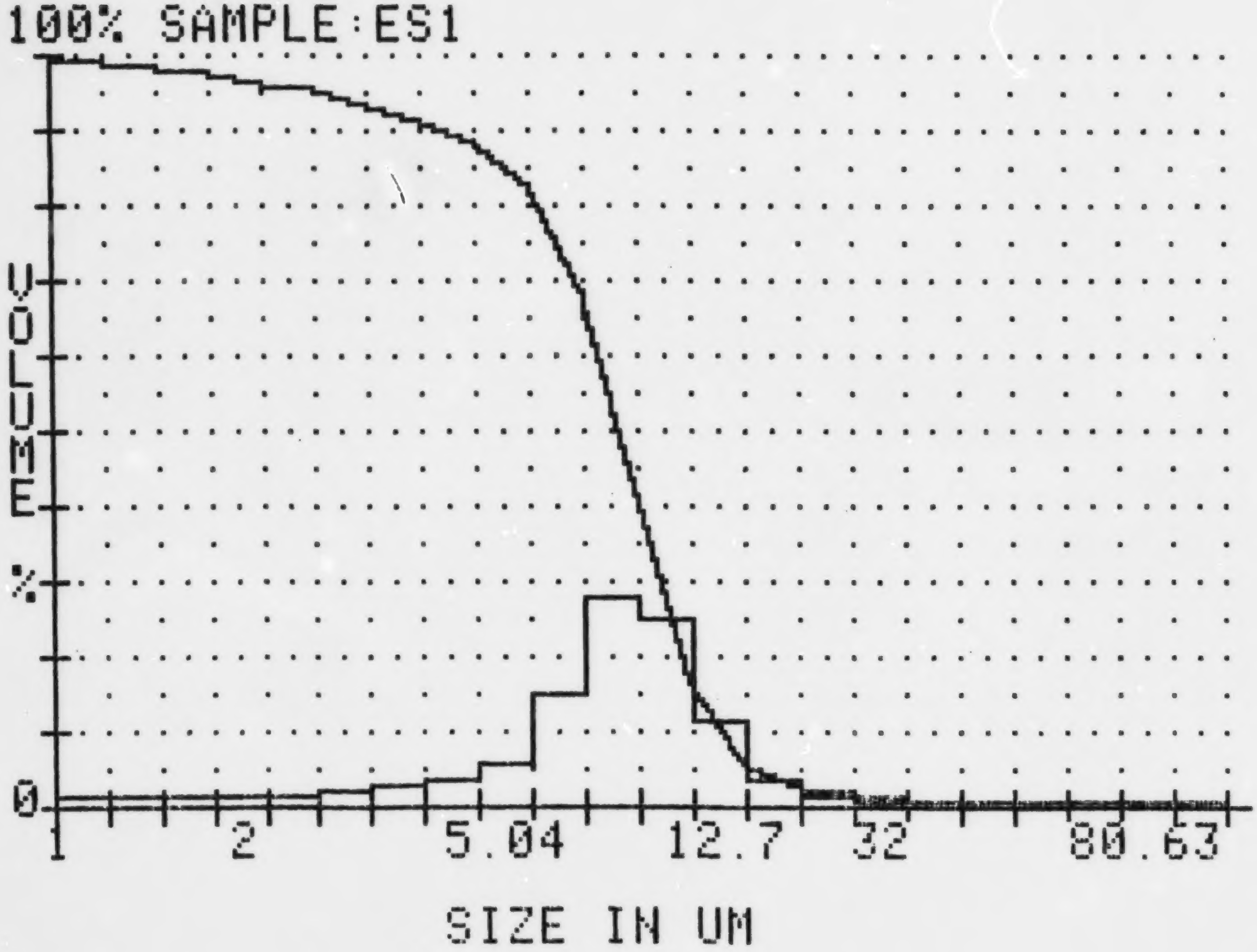


```
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

DATE: JAN 26 88
SAMPLE: ES1 (CAUSTIC/SODA ASH LEACH TAILS)
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 15 SEC SONIC PROBE
****************************************
CH.#    SIZE          DIFF      CUM
                      VOL %     VOL %
****************************************
1       1             1.1       100
2       1.26          .95       98.9
3       1.59          .73       97.95
4       2             1.07      97.21
5       2.52          1.16      96.14
6       3.17          1.47      94.98
7       4             2.2       93.51
8       5.04          3.24      91.31
9       6.35          5.36      88.06
10      8             14.69     82.7
11      10.08         27.66     68.01
12      12.7          24.56     40.35
13      16            11.14     15.79
14      20.16         2.94      4.65
15      25.4          .86       1.7
16      32            .51       .84
17      40.32         .2        .33
18      50.8          .08       .13
19      64            .05       .05
20      80.63         0         0
21      101.59        0         0
22      128           0         0


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                   10.62 UM
MEDIAN:                 11.72 UM
MODE                    12.15 UM
STANDARD DEVIATION:     1.76 UM
COEF. VAR.:             16.54 %
SKEWNESS:               .75 NEGATIVE
KURTOSIS:               2.04 PLATYKURTIC
```

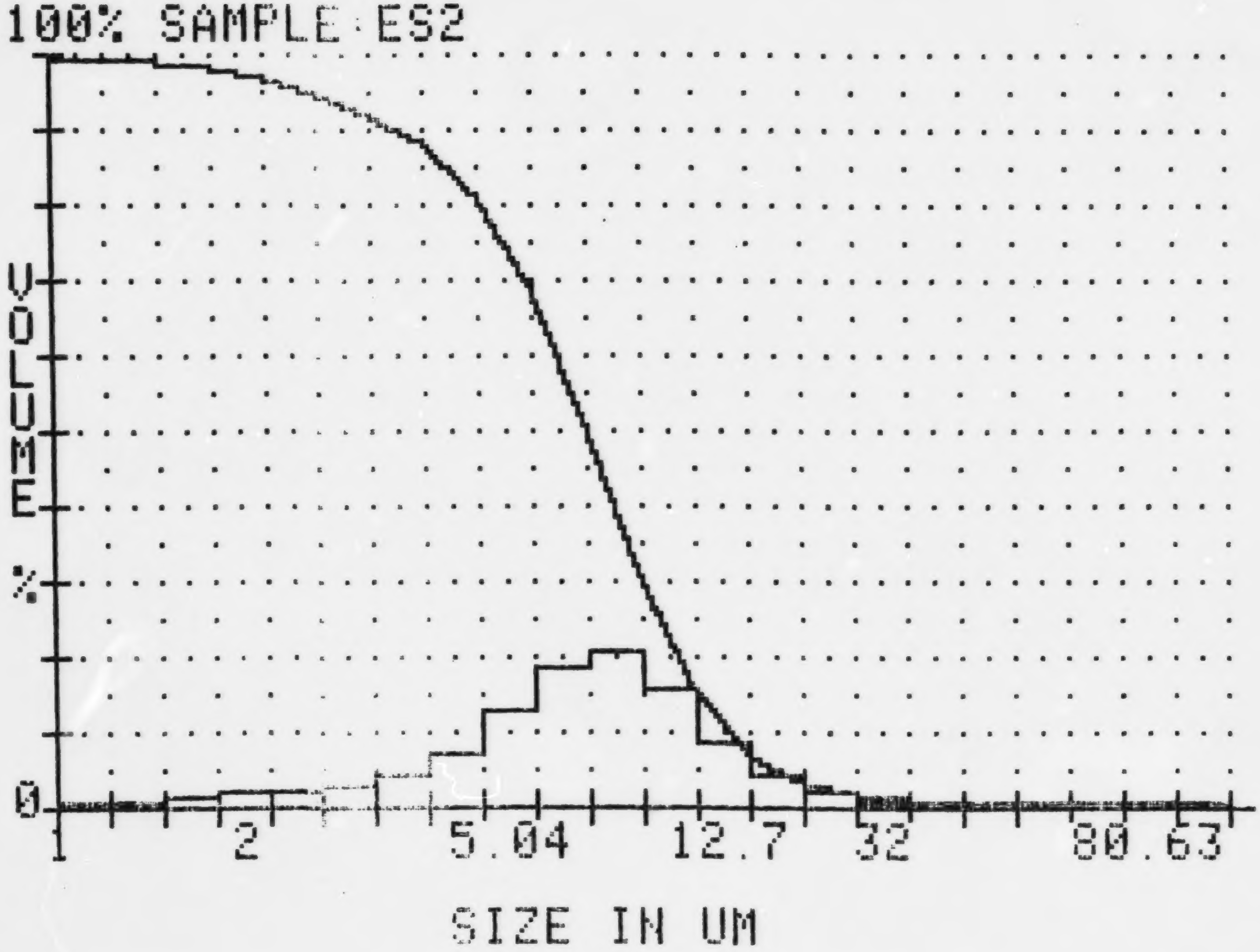

100% SAMPLE:ES1
VOLUME %
0
1
2
5.04
12.7
32
80.63
SIZE IN UM

```
ONTARIO RESEARCH
FINE PARTICLE LABORATORY

DATE: JAN 26 88
SAMPLE: ES2  CAUSTIC LEACH TAILS
ELECTROLYTE: ISOTON
DISPERSANT: IA
EQUIPMENT: TA II
APERTURES: 70  280
OPERATOR: SMITH
COMMENTS: 15 SEC SONIC PROBE
****************************************
CH.#    SIZE          DIFF        CUM
                      VOL %       VOL %
****************************************
1       1             .29         100
2       1.26          .68         99.71
3       1.59          .94         99.03
4       2             1.44        98.08
5       2.52          1.76        96.64
6       3.17          2.81        94.88
7       4             4.17        92.07
8       5.04          6.98        87.9
9       6.35          12.23       80.92
10      8             18.43       68.68
11      10.08         20.32       50.26
12      12.7          15.34       29.94
13      16            8.26        14.6
14      20.16         3.69        6.34
15      25.4          1.53        2.66
16      32            .52         1.13
17      40.32         .23         .61
18      50.8          0           .38
19      64            .31         .38
20      80.63         0           .07
21      101.59        0           .07
22      128           .07         .07


****************************************
        VOLUME % STATISTICS
****************************************

MEAN:                       9.5 UM
MEDIAN:                     10.11 UM
MODE                        10.74 UM
STANDARD DEVIATION:         1.8 UM
COEF. VAR.:                 18.92 %
SKEWNESS:                   .89 NEGATIVE
KURTOSIS:                   1.73 PLATYKURTIC
```


100% SAMPLE ES2
VOLUME
%
0
1
2
5.04
12.7
32
80.63
SIZE IN UM

CAUSTIC/SODA ASH LEACH TAILS

```
                  Micromeritics Instrument Corporation
                                                                  PAGE 24
ASAP 2400 V2.00

SAMPLE DIRECTORY/NUMBER: DATA1    /146              START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226  AB                       COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                         REPRT 08:28:12 02/04/88
OPERATOR: TK                                        SAMPLE WT:     0.4741 g
STATION NUMBER: 4       EQUIL INTERVAL:    10 sec   FREE SPACE:  61.6550 cc

                            SUMMARY REPORT

                                 AREA

BET SURFACE AREA:                                          38.1591    sq. m/g

LANGMUIR SURFACE AREA:                                     59.7863    sq. m/g

SINGLE POINT SURFACE AREA AT P/Po 0.2988:                  37.8623    sq. m/g

BJH CUMULATIVE ADSORPTION SURFACE AREA OF PORES
 BETWEEN      17.0000 AND   3000.0000 A  DIAMETER:         30.0564    sq. m/g

BJH CUMULATIVE DESORPTION SURFACE AREA OF PORES
 BETWEEN      17.0000 AND   3000.0000 A  DIAMETER:         38.6320    sq. m/g


                                VOLUME

SINGLE POINT TOTAL PORE VOLUME OF PORES LESS THAN
   2366.2947 A  DIAMETER AT P/Po 0.9918:                   0.079334 cc/g

BJH CUMULATIVE ADSORPTION PORE VOLUME OF PORES
 BETWEEN      17.0000 AND   3000.0000 A  DIAMETER:         0.074271 cc/g

BJH CUMULATIVE DESORPTION PORE VOLUME OF PORES
 BETWEEN      17.0000 AND   3000.0000 A  DIAMETER:         0.073869 cc/g


                              PORE SIZE

AVERAGE PORE DIAMETER (4V/A BY BET):                       83.1614    A

BJH ADSORPTION AVERAGE PORE DIAMETER (4V/A):               98.8422    A

BJH DESORPTION AVERAGE PORE DIAMETER (4V/A):               76.4847    A
```

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SAMPLE DIRECTORY/NUMBER: DATA1   /146              START 15:05:03 02/03/88
SAMPLE ID: ES1   MAL 226  AB                       COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:28:12 02/04/88
OPERATOR: TK                                       SAMPLE WT:     0.4741 g
STATION NUMBER: 4       EQUIL INTERVAL:    10 sec  FREE SPACE:  61.6550 cc
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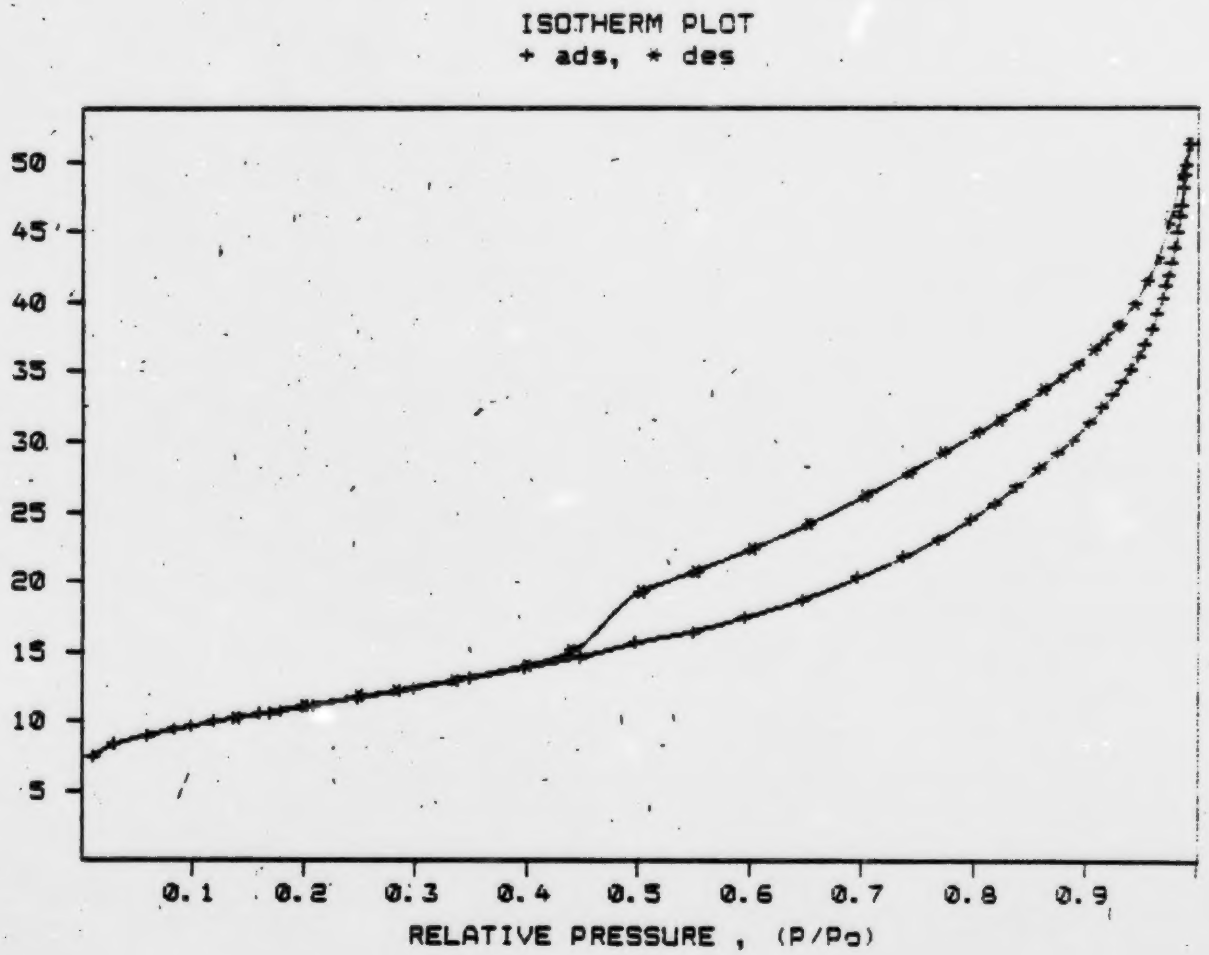

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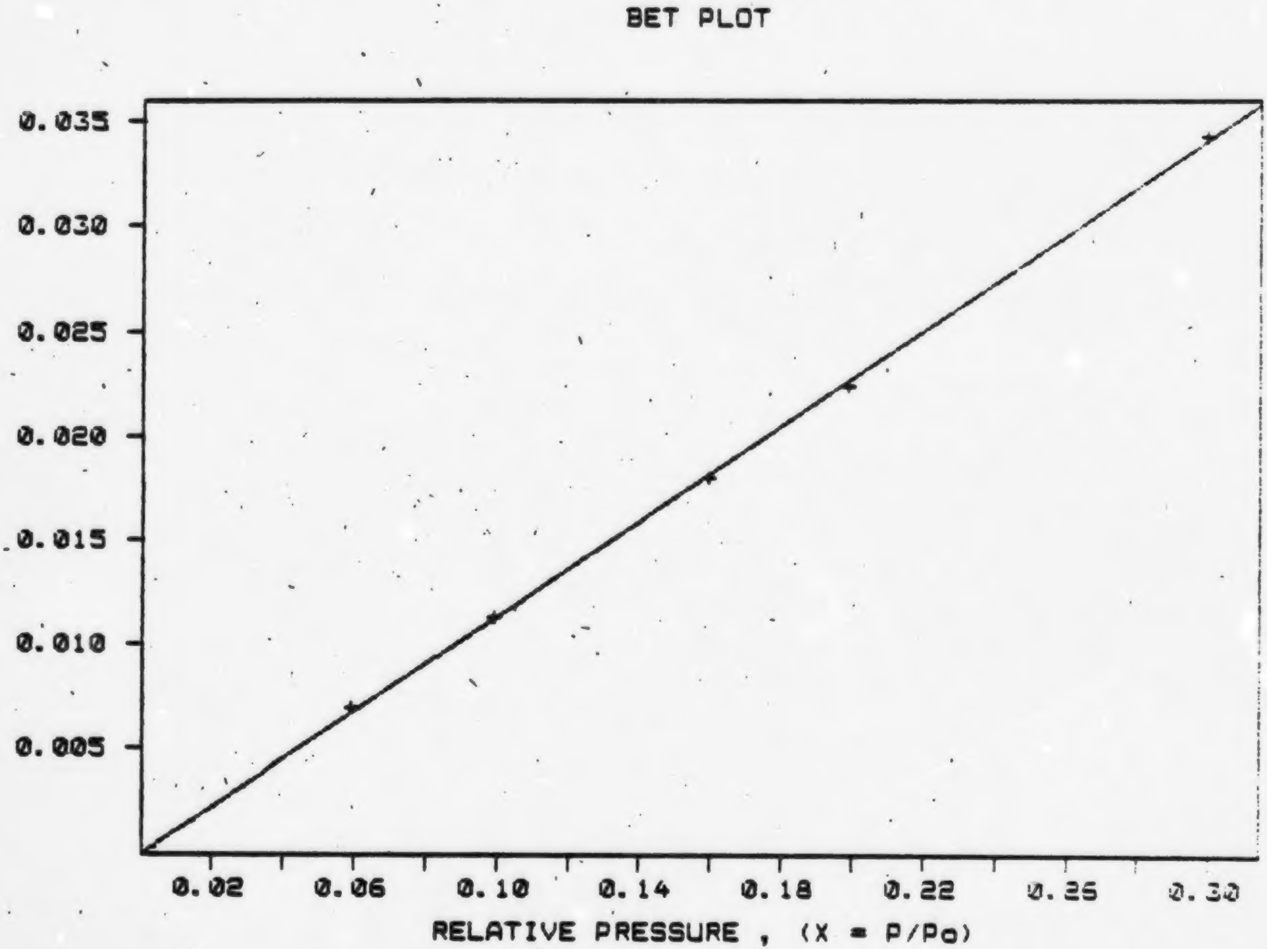
ASAP 2400 V2.00
                                                                                     PAGE   5
SAMPLE DIRECTORY/NUMBER: DATA1    /146
SAMPLE ID: ES1    MAL 226  AB                                      START 15:05:03 02/03/88
SUBMITTER: ONTARIO RESEARCH                                        COMPL 23:21:37 02/03/88
OPERATOR: TK                                                       REPRT 08:28:12 02/04/88
STATION NUMBER: 4          EQUIL INTERVAL:     10 sec              SAMPLE WT:      0.4741 g
                                                                   FREE SPACE:  61.6550 cc

                                  BET SURFACE AREA REPORT

        BET SURFACE AREA:                     38.1591    +/-     0.4778    sq. m/g
        SLOPE:                                 0.114068 +/-     0.001405
        Y-INTERCEPT:                           0.000012 +/-     0.000257
        C:                                  9600.642578  -
        VM:                                    8.765753 cc/g STP
        CORRELATION COEFFICIENT: 9.99772E-01

           RELATIVE                VOL ADSORBED
           PRESSURE                 (cc/g STP)                    1/
                                                           [VA(Po/P - 1)]
            0.0593
            0.0993                   9.0438
            0.1593                   9.6918                   0.006970
            0.1988                  10.5285                   0.011373
            0.2988                  11.0712                   0.017995
                                    12.4140                   0.022408
                                                              0.034334
```

```
SAMPLE DIRECTORY/NUMBER: DATA1    /146                    START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                            COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                               REPRT 08:28:12 02/04/88
OPERATOR: TK                                              SAMPLE WT:    0.4741 g
STATION NUMBER: 4         EQUIL INTERVAL:     10 sec      FREE SPACE:  61.6550 cc
```



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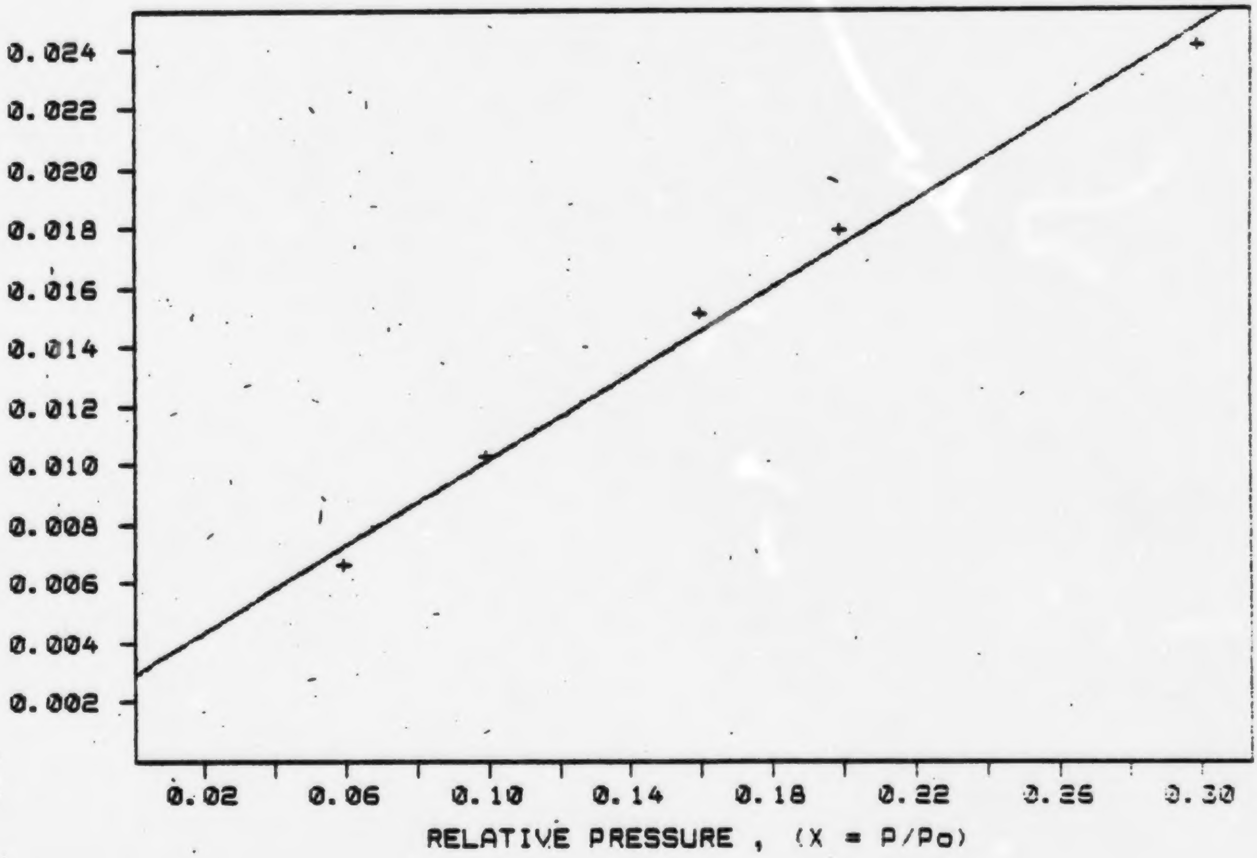
SAMPLE DIRECTORY/NUMBER: DATA1    /146                START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                        COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                           REPRT 08:28:12 02/04/88
OPERATOR: TK                                          SAMPLE WT:     0.4741 g
STATION NUMBER: 4      EQUIL INTERVAL:    10 sec      FREE SPACE:  61.6550 cc
```

LANGMUIR PLOT



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SAMPLE DIRECTORY/NUMBER: DATA1    /146             START 15:05:03 02/03/88
SAMPLE ID: ES1   MAL 226  AB                       COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:28:12 02/04/88
OPERATOR: TK                                       SAMPLE WT:    0.4741 g
STATION NUMBER: 4      EQUIL INTERVAL:    10 sec   FREE SPACE:  61.6550 cc

                        LANGMUIR SURFACE AREA REPORT

      LANGMUIR SURFACE AREA:      59.7863   +/-     3.1523   sq. m/g
      SLOPE:                      0.072813 +/-     0.003839
      Y-INTERCEPT:                0.002916 +/-     0.000703
      C:                         24.971430
      VM:                        13.733885 cc/g STP
      CORRELATION COEFFICIENT: 9.95856E-01

         RELATIVE            VOL ADSORBED                1/
         PRESSURE            (cc/g STP)              [VA*Po/P]

          0.0593                9.0438                0.006556
          0.0993                9.6918                0.010244
          0.1593               10.5285                0.015129
          0.1988               11.0712                0.017954
          0.2988               12.4140                0.024073
```

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SAMPLE DIRECTORY/NUMBER: DATA1    /146          START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                  COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                     REPRT 08:28:12 02/04/88
OPERATOR: TK                                    SAMPLE WT:      0.4741 g
STATION NUMBER: 4        EQUIL INTERVAL:    10 sec  FREE SPACE:  61.6550 cc

                  BJH ADSORPTION PORE DISTRIBUTION REPORT

 PORE DIAMETER     AVERAGE   INCREMENTAL CUMULATIVE  INCREMENTAL CUMULATIVE
     RANGE        DIAMETER   PORE VOLUME PORE VOLUME  PORE AREA   PORE AREA
     (A )           (A )        (cc/g)      (cc/g)    (sq. m/g)   (sq. m/g)

2366.3- 1851.1     2045.7     0.002444    0.002444      0.048       0.048
  51.1- 1733.0     1788.1     0.001115    0.003558      0.025       0.073
1733.0- 1518.1     1611.1     0.001546    0.005104      0.038       0.111
1518.1- 1305.0     1395.2     0.002140    0.007243      0.061       0.172
  05.0- 1218.6     1258.8     0.001053    0.008297      0.033       0.206
  18.6- 1044.2     1117.6     0.001868    0.010165      0.067       0.273
1044.2-  932.4      981.8     0.001812    0.011977      0.074       0.347
  32.4-  830.3      875.3     0.001710    0.013687      0.078       0.425
  30.3-  741.7      780.9     0.001558    0.015244      0.080       0.505
 741.7-  679.0      707.5     0.001372    0.016616      0.078       0.582
 679.0-  614.9      643.7     0.001304    0.017920      0.081       0.663
 614.9-  539.0      571.8     0.001942    0.019863      0.136       0.799
 539.0-  477.4      504.3     0.001899    0.021762      0.151       0.950
 477.4-  419.0      444.2     0.001921    0.023683      0.173       1.123
 419.0-  374.2      393.9     0.001658    0.025342      0.168       1.291
 374.2-  333.2      351.2     0.001685    0.027027      0.192       1.483
 333.2-  299.0      314.1     0.001617    0.028643      0.206       1.629
 299.0-  268.6      282.1     0.001640    0.030283      0.233       1.921
 268.6-  239.1      252.0     0.001777    0.032060      0.282       2.203
 239.1-  214.1      225.1     0.001747    0.033807      0.310       2.514
 214.1-  185.8      197.8     0.002387    0.036194      0.483       2.997
 185.8-  165.6      174.4     0.002052    0.038246      0.471       3.467
 165.6-  147.6      155.4     0.002023    0.040269      0.521       3.988
 147.6-  130.4      137.8     0.002513    0.042782      0.729       4.717
 130.4-  116.4      122.5     0.002367    0.045148      0.773       5.490
 116.4-  104.6      109.8     0.002340    0.047488      0.852       6.342
 104.6-   91.5       97.1     0.002959    0.050447      1.219       7.562
  91.5-   80.7       85.3     0.002717    0.053164      1.274       8.835
  80.7-   69.8       74.3     0.003122    0.056286      1.680      10.515
  69.8-   59.7       63.8     0.003106    0.059392      1.947      12.462
  59.7-   51.5       54.9     0.002640    0.062032      1.924      14.386
  51.5-   45.5       48.1     0.002001    0.064034      1.665      16.051
  45.5-   40.1       42.4     0.001434    0.065467      1.352      17.403
  40.1-   35.8       37.7     0.001996    0.067464      2.119      19.522
  35.8-   32.1       33.7     0.001395    0.068859      1.656      21.178
  32.1-   28.8       30.2     0.001258    0.070117      1.665      22.843
  28.8-   25.8       27.1     0.001265    0.071382      1.868      24.711
  25.8-   23.0       24.2     0.001060    0.072442      1.750      26.461
  23.0-   21.0       21.9     0.000771    0.073213      1.406      27.867
  21.0-   20.5       20.8     0.000123    0.073336      0.237      28.104
  20.5-   19.6       20.0     0.000411    0.073747      0.822      28.926
```

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SAMPLE DIRECTORY/NUMBER: DATA1   /146                 START 15:05:03 02/03/88
SAMPLE ID: ES1   MAL 226  AB                          COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                           REPRT 08:29:12 02/04/88
OPERATOR: TK                                          SAMPLE WT:    0.4741 g
STATION NUMBER: 4      EQUIL INTERVAL:    10 sec      FREE SPACE:  61.6550 cc

                    BJH ADSORPTION PORE DISTRIBUTION REPORT

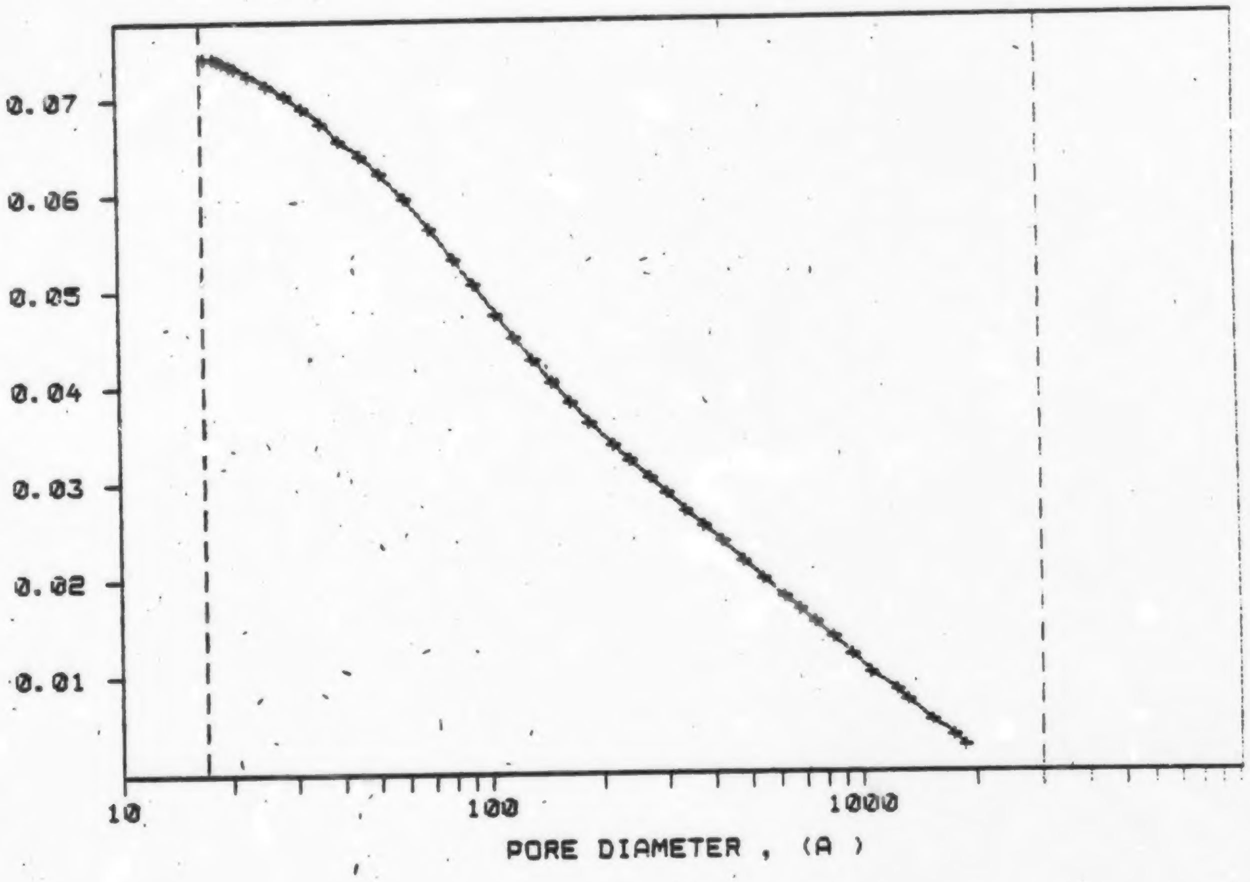
 PORE DIAMETER      AVERAGE   INCREMENTAL CUMULATIVE  INCREMENTAL CUMULATIVE
    RANGE           DIAMETER  PORE VOLUME PORE VOLUME  PORE AREA   PORE AREA
     (A )             (A )       (cc/g)      (cc/g)    (sq. m/g)   (sq. m/g)

   19.6-    19.1      19.3     0.000101    0.073848       0.210       29.136
   19.1-    18.6      18.8     0.000198    0.074046       0.420       29.556
   18.6-    17.5      18.0     0.000225    0.074271       0.500       30.056
```

```
ASAP 2400 V2.00

SAMPLE DIRECTORY/NUMBER: DATA1    /146            START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                     COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:28:12 02/04/88
OPERATOR: TK                                       SAMPLE WT:     0.4741 g
STATION NUMBER: 4      EQUIL INTERVAL:    10 sec   FREE SPACE:   61.6550 cc
```

CUMULATIVE ADSORPTION PORE VOLUME PLOT



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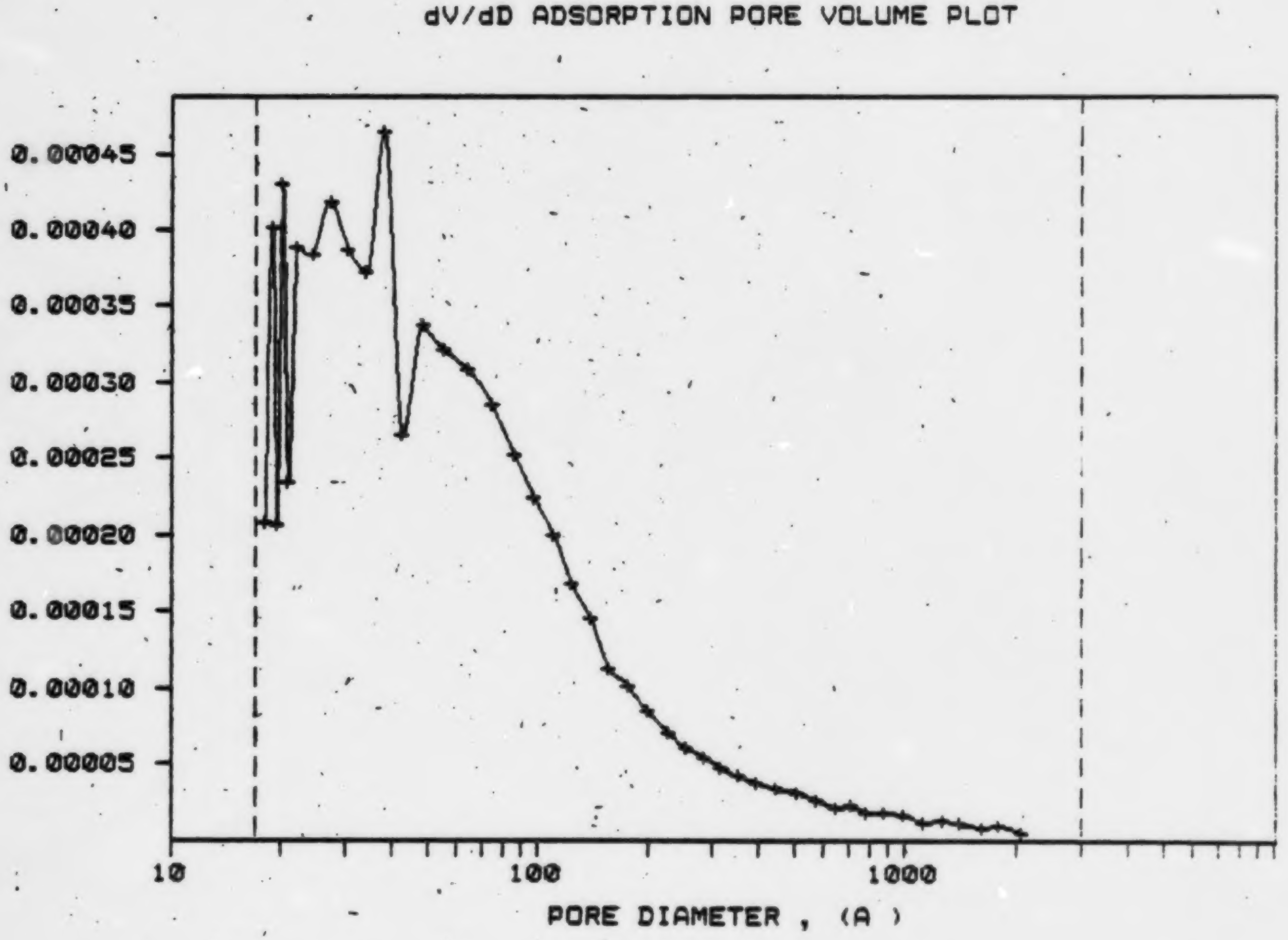
                    Micromeritics Instrument Corporation
SAP 2400 V2.00                                                        PAGE 12

SAMPLE DIRECTORY/NUMBER: DATA1    /146              START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                      COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                         REPRT 08:28:12 02/04/88
OPERATOR: TK                                        SAMPLE WT:     0.4741 g
STATION NUMBER: 4        EQUIL INTERVAL:    10 sec  FREE SPACE:  61.6550 cc
```


dV/dD ADSORPTION PORE VOLUME PLOT

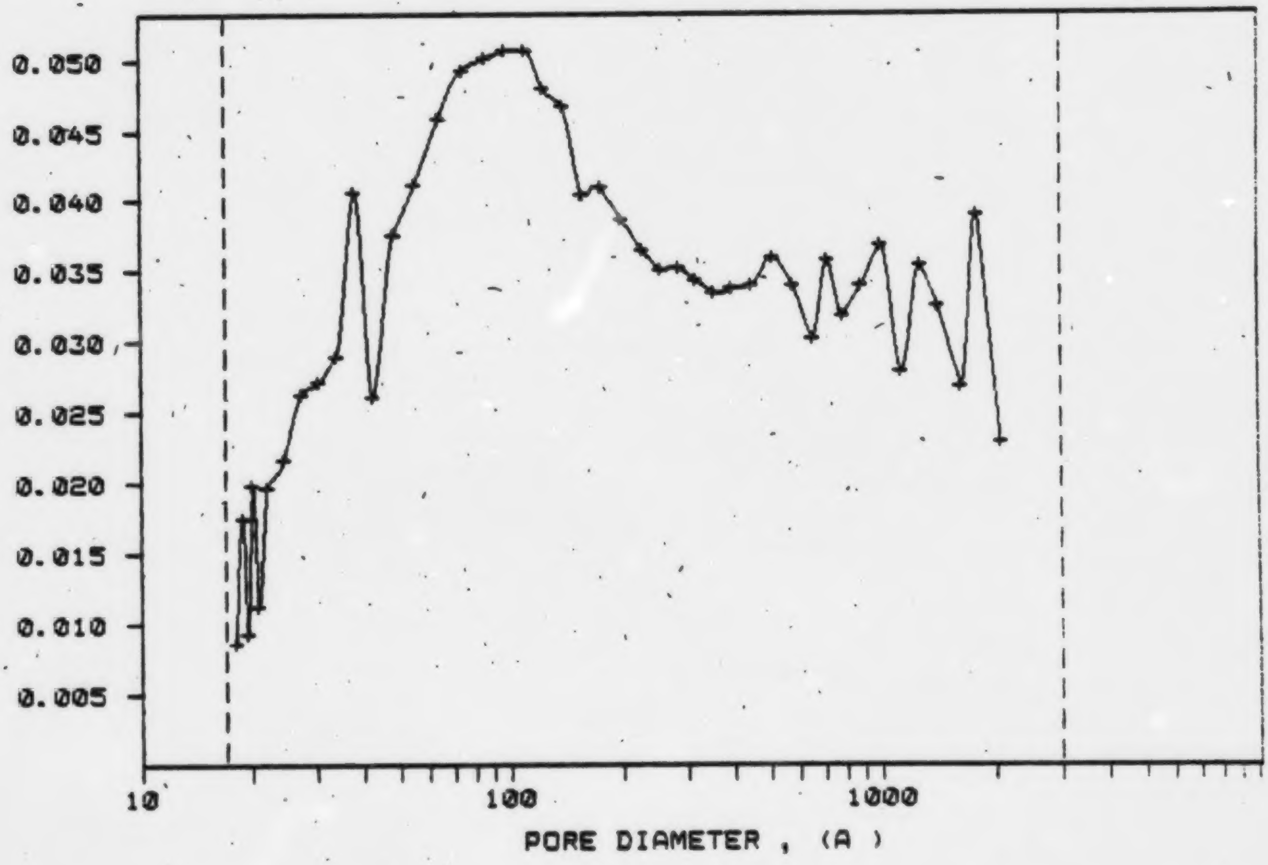
Micromeritics Instrument Corporation

ASAP 2400 V2.00 PAGE 13

SAMPLE DIRECTORY/NUMBER: DATA1 /146
SAMPLE ID: ES1 MAL 226 AB
SUBMITTER: ONTARIO RESEARCH
OPERATOR: TK
STATION NUMBER: 4 EQUIL INTERVAL: 10 sec

START 15:05:03 02/03/88
COMPL 23:21:37 02/03/88
REPRT 08:28:12 02/04/88
SAMPLE WT: 0.4741 g
FREE SPACE: 61.6550 cc

dV/dlog(D) ADSORPTION PORE VOLUME PLOT



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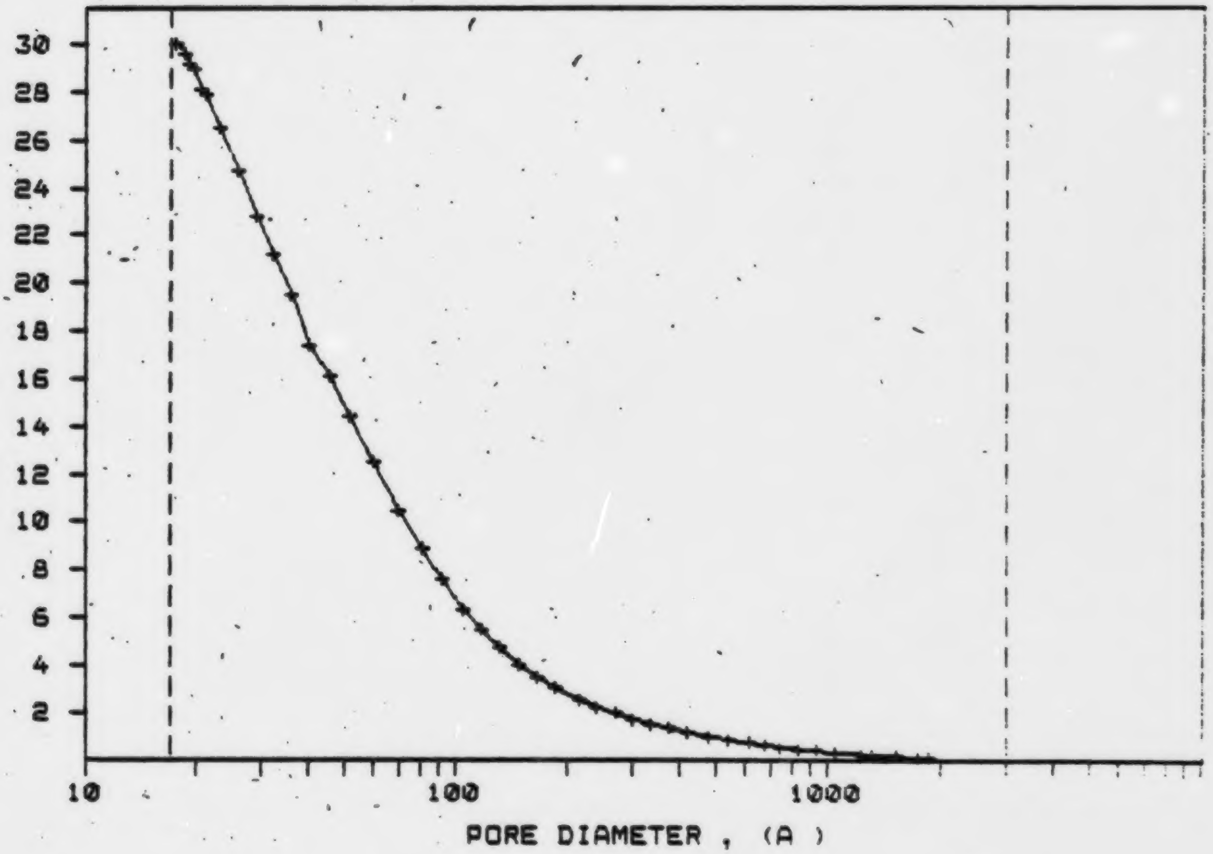
AN LE DIRECTORY/NUMBER: DATA1    /146           START 15:05:03 02/03/88
AMPLE ID: ES1   MAL 226  AB                     COMPL 23:21:37 02/03/88
UBMITTER: ONTARIO RESEARCH                      REPRT 08:28:12 02/04/88
PE ATOR: TK                                     SAMPLE WT:     0.4741 g
TATION NUMBER: 4      EQUIL INTERVAL:   10 sec  FREE SPACE:   61.6550 cc
```

CUMULATIVE ADSORPTION PORE AREA PLOT



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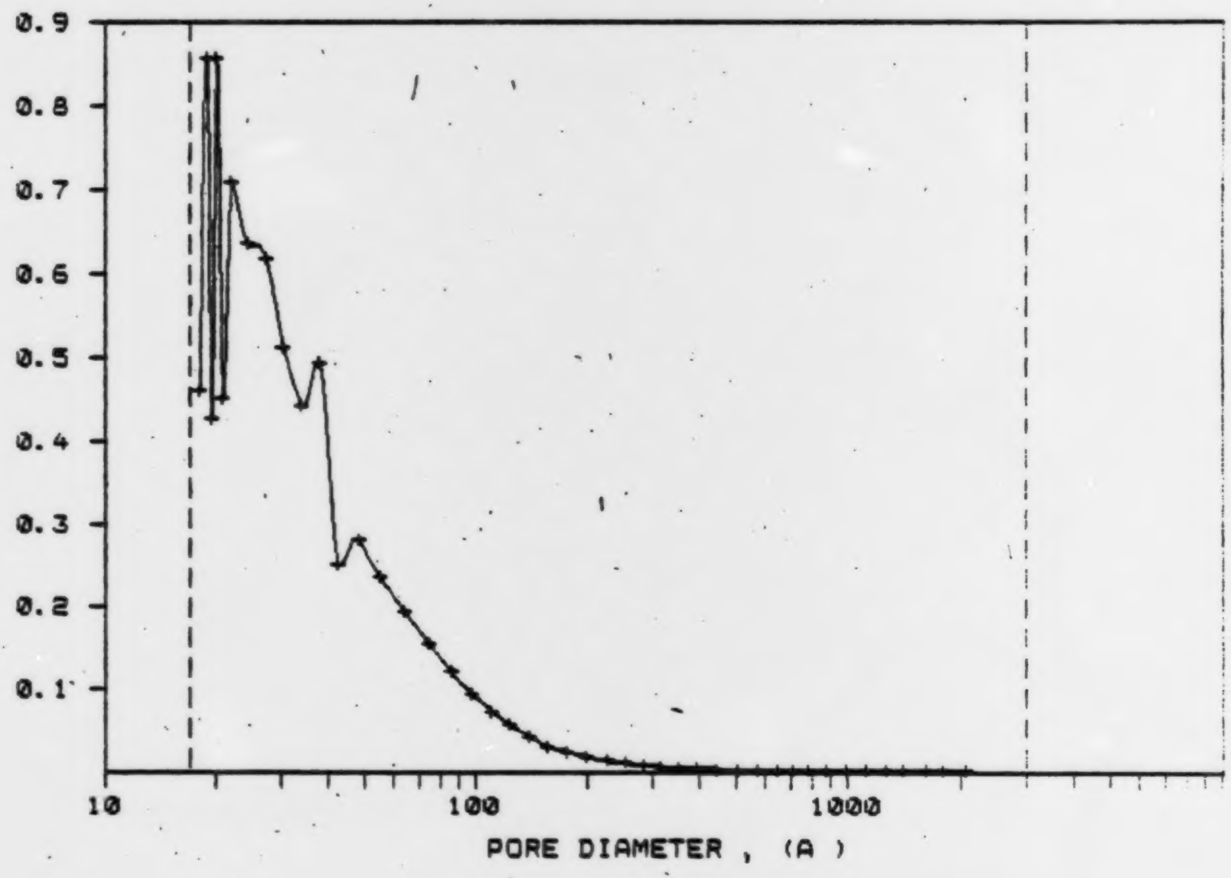
                        Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                          PAGE 15

SAMPLE DIRECTORY/NUMBER: DATA1    /146                START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                        COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                           REPRT 08:28:12 02/04/88
OPERATOR: TK                                          SAMPLE WT:     0.4741 g
STATION NUMBER: 4        EQUIL INTERVAL:     10 sec   FREE SPACE:   61.6550 cc
```

dA/dD ADSORPTION PORE AREA PLOT



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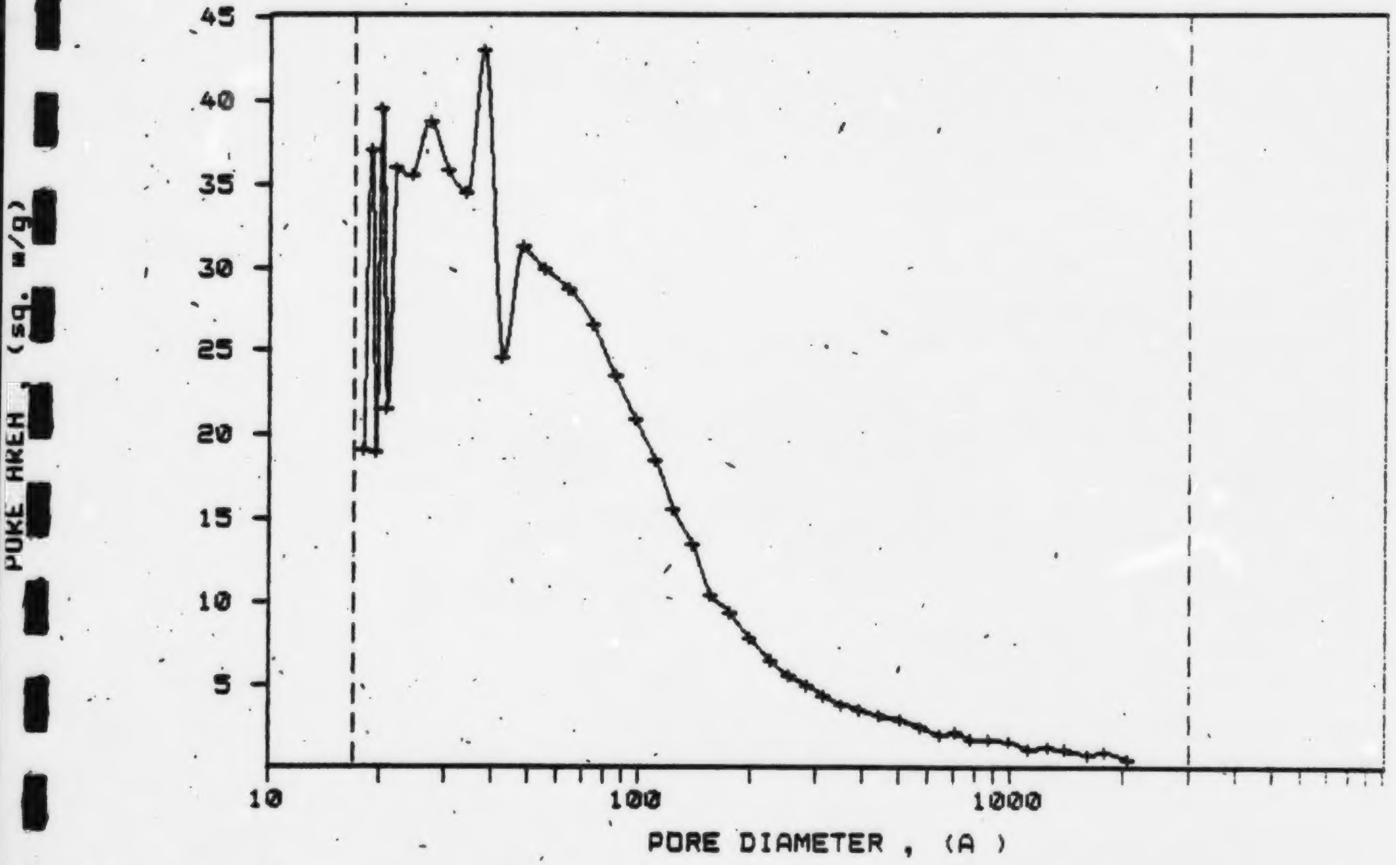
                    Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                      PAGE 16

SAMPLE DIRECTORY/NUMBER: DATA1    /146                   START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                           COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                              REPRT 08:28:12 02/04/88
OPERATOR: TK                                             SAMPLE WT:     0.4741 g
STATION NUMBER: 4         EQUIL INTERVAL:     10 sec     FREE SPACE:  61.6550 cc
```

dA/dlog(D) ADSORPTION PORE AREA PLOT



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                     Micromeritics Instrument Corporation
                                                                        PAGE 17
5AP 2400 V2.00

AMPLE DIRECTORY/NUMBER: DATA1    /146                  START 15:05:03 02/03/88
AMPLE ID: ES1   MAL 226  AB                            COMPL 23:21:37 02/03/88
UBMITTER: ONTARIO RESEARCH                             REPRT 08:28:12 02/04/88
PERATOR: TK                                            SAMPLE WT:      0.4741 g
TATION NUMBER: 4        EQUIL INTERVAL:     10 sec     FREE SPACE:   61.6550 cc

                     BJH DESORPTION PORE DISTRIBUTION REPORT

PORE DIAMETER        AVERAGE    INCREMENTAL CUMULATIVE  INCREMENTAL CUMULATIVE
   RANGE             DIAMETER   PORE VOLUME PORE VOLUME  PORE AREA   PORE AREA
    (A )               (A )       (cc/g)      (cc/g)     (sq. m/g)   (sq. m/g)

12 1.8-   855.3       970.1     0.004142    0.004142       0.171       0.171
 55.3-    737.8       787.6     0.001570    0.005712       0.080       0.251
737.8-    559.5       623.6     0.003819    0.009532       0.245       0.496
 59.5-    442.4       486.8     0.003054    0.012586       0.251       0.747
 42.4-    354.7       388.5     0.002805    0.015391       0.289       1.035
354.7-    289.2       314.9     0.002695    0.018085       0.342       1.378
 89.2-    278.9       283.8     0.000467    0.018552       0.066       1.443
 78.9-    247.0       260.8     0.001459    0.020011       0.224       1.667
247.0-    222.1       233.1     0.001481    0.021493       0.254       1.921
 22.1-    192.3       204.9     0.002026    0.023518       0.395       2.317
 92.3-    170.1       179.7     0.001809    0.025328       0.403       2.719
170.1-    152.1       160.0     0.001719    0.027047       0.430       3.149
152.1-    133.7       141.6     0.002106    0.029153       0.595       3.744
 33.7-    119.2       125.5     0.002116    0.031269       0.674       4.419
119.2-    107.1       112.4     0.002078    0.033347       0.739       5.158
107.1-     93.2        99.1     0.002960    0.036307       1.195       6.353
 93.2-     82.2        86.9     0.002919    0.039227       1.343       7.696
 82.2-     71.2        75.8     0.003728    0.042955       1.967       9.663
 71.2-     60.6        64.9     0.004462    0.047417       2.750      12.413
 60.6-     52.4        55.8     0.004006    0.051423       2.871      15.285
 52.4-     45.9        48.7     0.003552    0.054975       2.920      18.204
 45.9-     40.6        42.9     0.003340    0.058315       3.116      21.320
 40.6-     35.2        37.5     0.012457    0.070772      13.301      34.621
 35.2-     32.2        33.5     0.001842    0.072614       2.197      36.818
 32.2-     27.9        29.7     0.000734    0.073348       0.989      37.806
 27.9-     24.9        26.2     0.000346    0.073694       0.528      38.334
 24.9-     23.1        23.9     0.000144    0.073838       0.241      38.576
 23.1-     20.6        21.7     0.000030    0.073869       0.056      38.632
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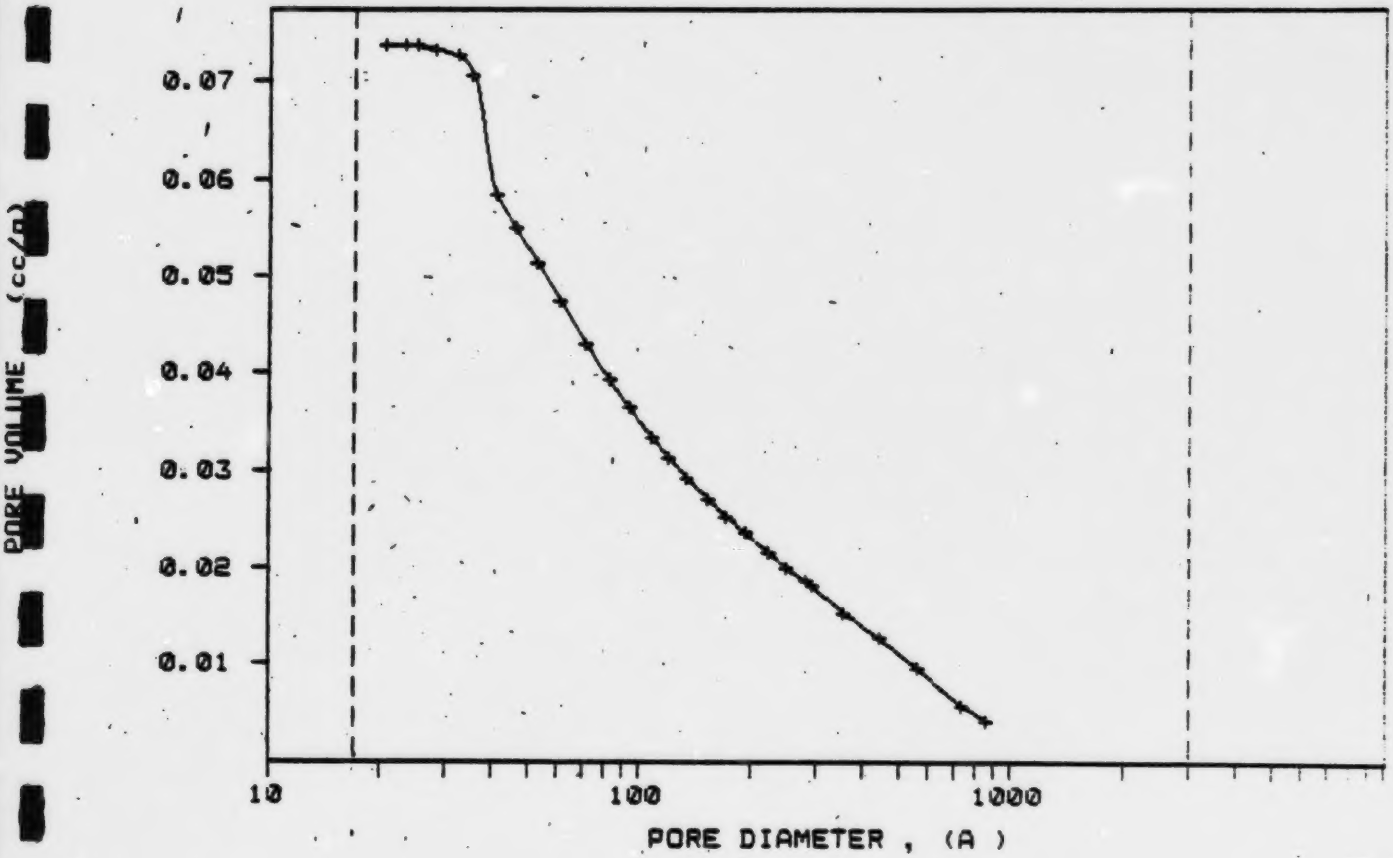
                    Micromeritics Instrument Corporation
SAP 2400 V2.00                                                      PAGE 18

AMPLE DIRECTORY/NUMBER: DATA1    /146             START 15:05:03 02/03/88
MPLE ID: ES1    MAL 226   AB                      COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                       REPRT 08:28:12 02/04/88
PERATOR: TK                                       SAMPLE WT:      0.4741 g
TATION NUMBER: 4        EQUIL INTERVAL:    10 sec  FREE SPACE:  61.6550 cc
```

CUMULATIVE DESORPTION PORE VOLUME PLOT



Micromeritics Instrument Corporation

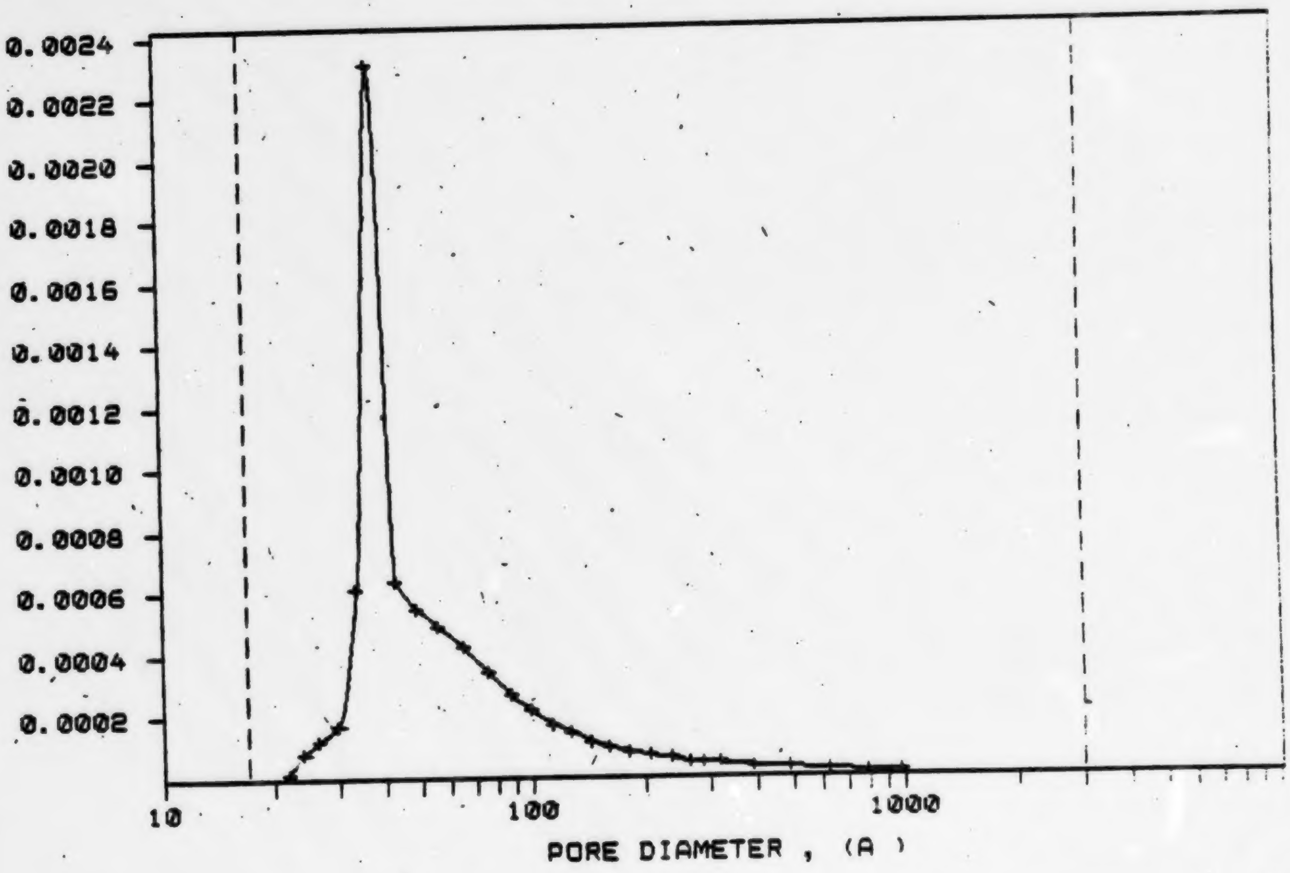
PAGE 19

SAP 2400 V2.00

A PLE DIRECTORY/NUMBER: DATA1 /146
AMPLE ID: ES1 MAL 226 AB
UBMITTER: ONTARIO RESEARCH
P RATOR: TK
T TION NUMBER: 4 EQUIL INTERVAL: 10 sec

START 15:05:03 02/03/88
COMPL 23:21:37 02/03/88
REPRT 08:28:12 02/04/88
SAMPLE WT: 0.4741 g
FREE SPACE: 61.6550 cc

dV/dD DESORPTION PORE VOLUME PLOT



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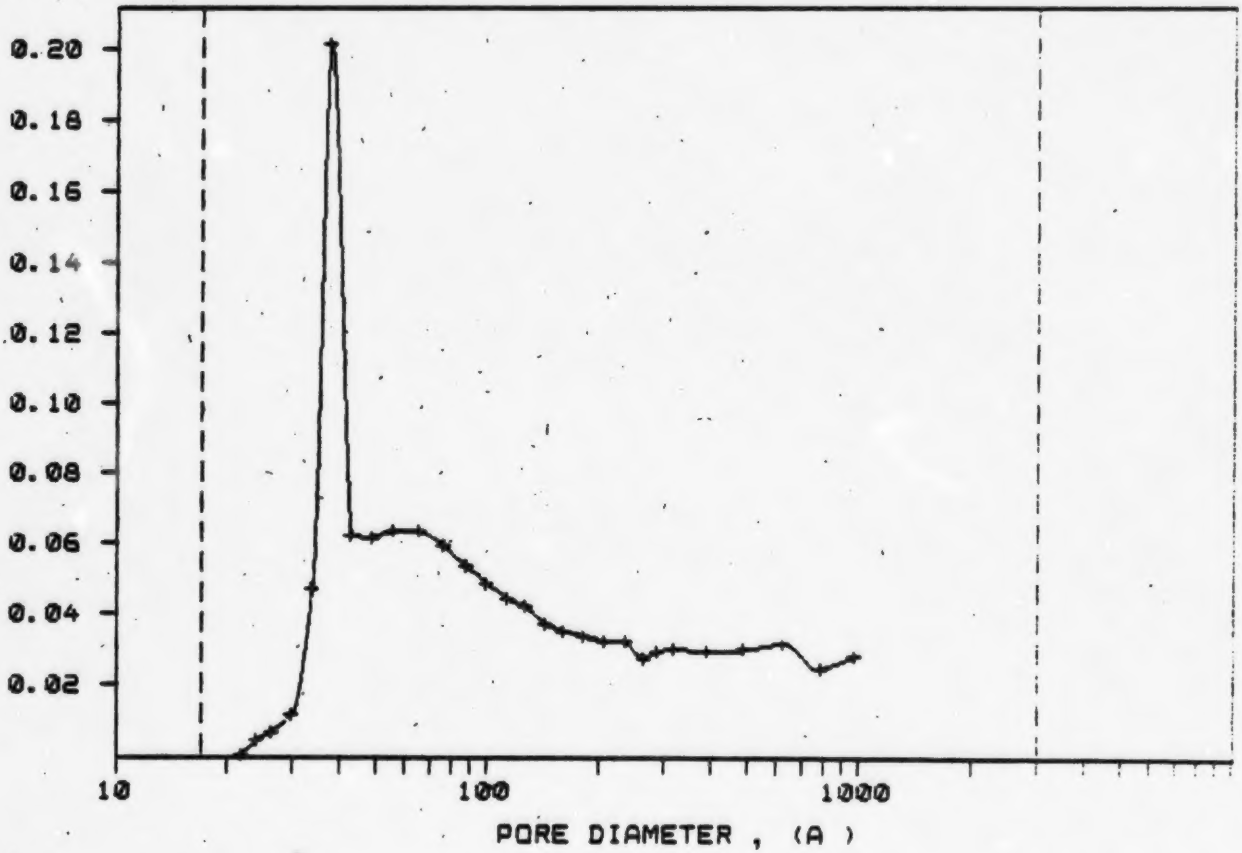
                    Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                      PAGE 20

SAMPLE DIRECTORY/NUMBER: DATA1    /146             START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                     COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:28:12 02/04/88
OPERATOR: TK                                       SAMPLE WT:     0.4741 g
STATION NUMBER: 4        EQUIL INTERVAL:    10 sec FREE SPACE:  61.6550 cc
```

dV/dlog(D) DESORPTION PORE VOLUME PLOT



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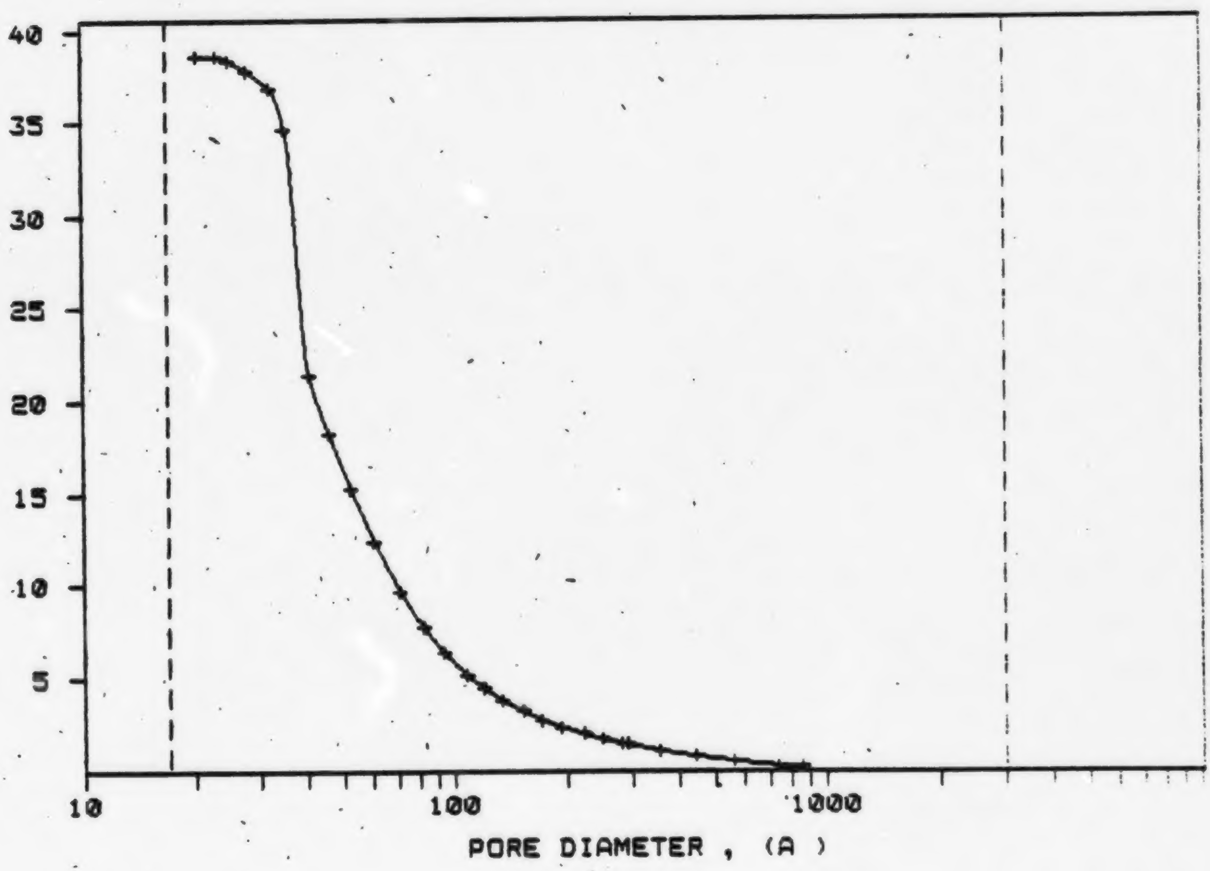
                  Micromeritics Instrument Corporation
SAP 2400 V2.00                                                    PAGE 21

AN LE DIRECTORY/NUMBER: DATA1    /146                  START 15:05:03 02/03/88
AMPLE ID: ES1    MAL 226   AB                          COMPL 23:21:37 02/03/88
UBMITTER: ONTARIO RESEARCH                             REPRT 08:28:12 02/04/88
PE ATOR: TK                                            SAMPLE WT:      0.4741 g
TATION NUMBER: 4        EQUIL INTERVAL:     10 sec     FREE SPACE:  61.6550 cc
```

CUMULATIVE DESORPTION PORE AREA PLOT



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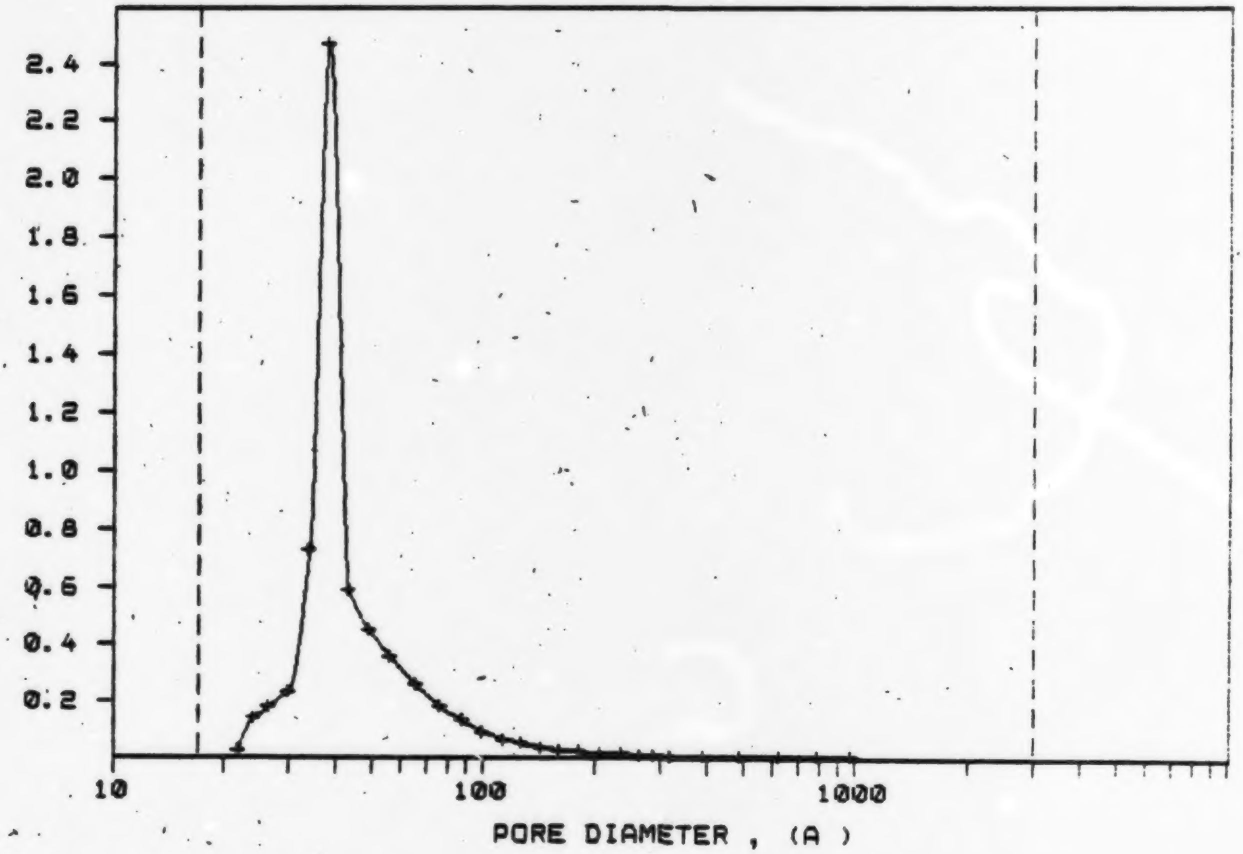
SA PLE DIRECTORY/NUMBER: DATA1   /146          START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                   REPRT 08:28:12 02/04/88
OP RATOR: TK                                  SAMPLE WT:     0.4741 g
ST TION NUMBER: 4       EQUIL INTERVAL:    10 sec   FREE SPACE:  61.6550 cc
```

dA/dD DESORPTION PORE AREA PLOT



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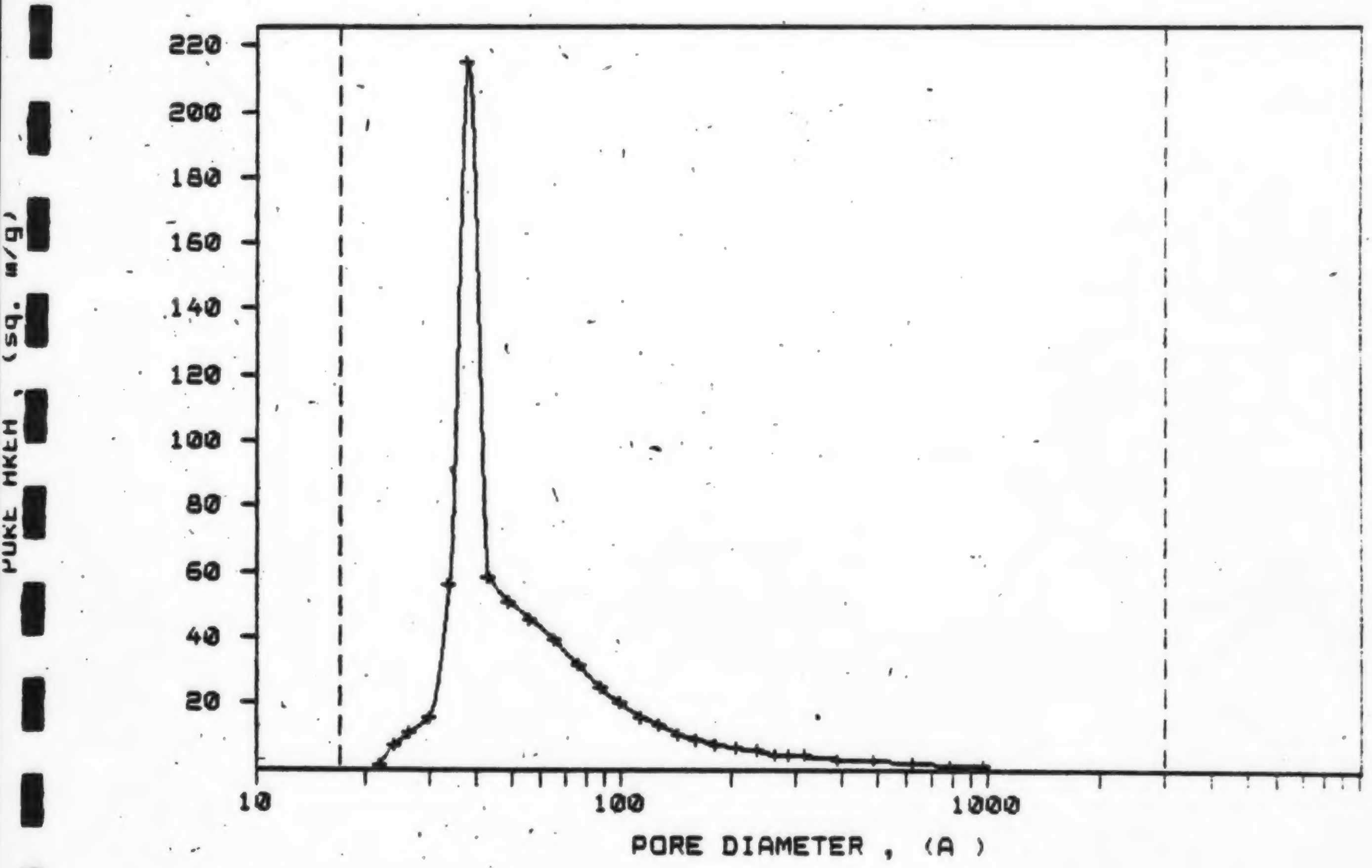
                    Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                        PAGE 23

SAMPLE DIRECTORY/NUMBER: DATA1    /146               START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                       COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                          REPRT 08:28:12 02/04/88
OPERATOR: TK                                         SAMPLE WT:     0.4741 g
STATION NUMBER: 4        EQUIL INTERVAL:     10 sec  FREE SPACE:   61.6550 cc
```

dA/dlog(D) DESORPTION PORE AREA PLOT



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                  Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                     PAGE  1

SAMPLE DIRECTORY/NUMBER: DATA1   /146               START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                      COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                         REPRT 08:28:12 02/04/88
OPERATOR: TK                                        SAMPLE WT:     0.4741 g
STATION NUMBER: 4       EQUIL INTERVAL:    10 sec   FREE SPACE:   61.6550 cc

                              ANALYSIS LOG

 RELATIVE     PRESSURE     VOL ADSORBED    ELAPSED TIME     SATURATION
 PRESSURE      (mmHg)      (cc/g STP)       (HR:MN)       PRESS.(mmHg)

                                              1:06           744.955
  0.0100        7.442        7.5739           1:48
  0.0298       22.209        8.3821           1:53
  0.0593       44.165        9.0438           1:57
  0.0835       62.170        9.4615           2:01
  0.0993       73.945        9.6918           2:06
  0.1191       88.713        9.9970           2:11
  0.1371      102.126       10.2458           2:15
  0.1593      118.635       10.5285           2:19
  0.1693      126.115       10.6724           2:24
  0.1794      133.596       10.7947           2:27
  0.1988      148.041       11.0712           2:31
  0.2093      155.897       11.1983           2:54
  0.2481      184.786       11.7251           2:58
  0.2988      222.554       12.4140           3:03
  0.3495      260.287       13.1504           3:06
  0.3983      296.610       13.8764           3:09
                                              3:10           744.696
  0.4479      333.514       14.6590           3:13
  0.4968      369.930       15.6251           3:18
  0.5487      408.548       16.4745           3:22
  0.5955      443.456       17.4959           3:25
  0.6474      482.040       18.8090           3:30
  0.6963      518.457       20.3158           3:35
  0.7368      548.568       21.8161           3:39
  0.7676      571.516       23.1293           3:46
  0.7972      593.499       24.5674           3:50
  0.8180      608.990       25.7147           3:55
  0.8381      623.903       26.8927           3:59
  0.8575      638.381       28.1582           4:04
  0.8736      650.292       29.2027           4:09
  0.8879      660.915       30.2705           4:14
  0.9033      672.375       31.5311           4:20
  0.9138      680.166       32.4684           4:26
  0.9237      687.505       33.4330           4:30
  0.9317      693.493       34.3315           4:34
  0.9390      698.901       35.2264           4:38
  0.9460      704.052       36.1689           4:42
  0.9520      708.494       37.1051           4:47
  0.9580      713.001       38.2002           4:51
  0.9630      716.671       39.2922           4:56
  0.9677      720.147       40.4207           5:02
```

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                   Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                   PAGE  2

SA PLE DIRECTORY/NUMBER: DATA1    /146              START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226   AB                      COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                         REPRT 08:28:12 02/04/88
OF RATOR: TK                                        SAMPLE WT:     0.4741 g
ST TION NUMBER: 4      EQUIL INTERVAL:     10 sec   FREE SPACE:  61.6550 cc

                              ANALYSIS LOG

 RELATIVE     PRESSURE     VOL ADSORBED    ELAPSED TIME      SATURATION
 PRESSURE      (mmHg)      (cc/g STP)        (HR:MN)        PRESS.(mmHg)

  0.9709       722.465       41.1863           5:06
  0.9734       724.332       41.9953           5:10
                                               5:11            744.127
  0.9763       726.457       42.9208           5:16
  0.9790       728.388       43.9436           5:22
  0.9813       730.062       45.0345           5:27
  0.9840       732.058       46.1683           5:32
  0.9851       732.831       46.8111           5:36
  0.9872       734.376       48.1231           5:41
  0.9888       735.535       49.0771           5:46
  0.9895       736.050       49.7677           5:49
  0.9918       737.724       51.2892           5:54
  0.9838       731.672       48.9729           6:00
  0.9770       726.585       46.4880           6:08
  0.9732       723.753       45.5574           6:12
  0.9644       717.121       43.3355           6:20
  0.9546       709.782       41.5914           6:27
  0.9429       701.026       40.0189           6:32
  0.9293       690.917       38.5369           6:37
  0.9266       688.857       38.2815           6:40
  0.9167       681.453       37.4876           6:44
  0.9069       674.178       36.6959           6:48
  0.8918       662.911       35.6262           6:53
  0.8771       651.902       34.6842           6:58
  0.8619       640.635       33.8008           7:02
  0.8422       625.959       32.7358           7:07
  0.8225       611.240       31.6893           7:11
  0.8019       595.942       30.6757           7:16
                                               7:16            743.145
  0.7720       573.701       29.2634           7:21
  0.7416       551.140       27.8995           7:26
  0.7023       521.931       26.2004           7:30
  0.6524       484.807       24.2070           7:36
  0.6022       447.507       22.4254           7:40
  0.5521       410.284       20.8395           7:44
  0.5021       373.141       19.3565           7:48
  0.4407       327.476       15.0711           7:57
  0.4003       297.512       14.0352           8:00
  0.3353       249.145       12.9987           8:04
  0.2835       210.651       12.2502           8:08
  0.2501       185.880       11.7884           8:11
  0.2001       148.686       11.1288           8:13
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                   Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                    PAGE  3

SAMPLE DIRECTORY/NUMBER: DATA1    /146              START 15:05:03 02/03/88
SAMPLE ID: ES1    MAL 226  AB                       COMPL 23:21:37 02/03/88
SUBMITTER: ONTARIO RESEARCH                         REPRT 08:28:12 02/04/88
OPERATOR: TK                                        SAMPLE WT:     0.4741 g
STATION NUMBER: 4       EQUIL INTERVAL:     10 sec  FREE SPACE:  61.6550 cc

                                ANALYSIS LOG

  RELATIVE     PRESSURE     VOL ADSORBED    ELAPSED TIME     SATURATION
  PRESSURE      (mmHg)      (cc/g STP)        (HR:MN)       PRESS.(mmHg)

   0.1401      104.125       10.3307           8:17
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                         CAUSTIC LEACH TAILS
                 Micromeritics Instrument Corporation
                                                                 PAGE 24
SAP 2400 V2.00

AMPLE DIRECTORY/NUMBER: DATA1    /147              START 15:11:20 02/03/88
AMPLE ID: ES2    MAL 227  B5                       COMPL 02:27:41 02/04/88
UBMITTER: ONTARIO RESEARCH                         REPRT 08:47:38 02/04/88
PERATOR: TK                                        SAMPLE WT:     0.4752 g
TATION NUMBER: 1        EQUIL INTERVAL:    10 sec  FREE SPACE:  55.6636 cc

                            SUMMARY REPORT

                                 AREA

BET SURFACE AREA:                                          59.3084   sq. m/g

LANGMUIR SURFACE AREA:                                     93.4709   sq. m/g

SINGLE POINT SURFACE AREA AT P/Po 0.2979:                  58.5368   sq. m/g

BJH CUMULATIVE ADSORPTION SURFACE AREA OF PORES
 BETWEEN      17.0000 AND    3000.0000 A  DIAMETER:        57.6766   sq. m/g

BJH CUMULATIVE DESORPTION SURFACE AREA OF PORES
 BETWEEN      17.0000 AND    3000.0000 A  DIAMETER:        75.5107   sq. m/g

                                VOLUME

SINGLE POINT TOTAL PORE VOLUME OF PORES LESS THAN
  6537.3003 A  DIAMETER AT P/Po 0.9971:                    0.178883 cc/g

BJH CUMULATIVE ADSORPTION PORE VOLUME OF PORES
 BETWEEN      17.0000 AND    3000.0000 A  DIAMETER:        0.176287 cc/g

BJH CUMULATIVE DESORPTION PORE VOLUME OF PORES
 BETWEEN      17.0000 AND    3000.0000 A  DIAMETER:        0.175481 cc/g

                              PORE SIZE

AVERAGE PORE DIAMETER (4V/A BY BET):                       120.6458    A

BJH ADSORPTION AVERAGE PORE DIAMETER (4V/A):               122.2589    A

BJH DESORPTION AVERAGE PORE DIAMETER (4V/A):                92.9570    A
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                      Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                        PAGE  4

SAMPLE DIRECTORY/NUMBER: DATA1    /147                START 15:11:20 02/03/88
SAMPLE ID: ES2   MAL 227  B5                          COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                           REPRT 08:47:38 02/04/88
OPERATOR: TK                                          SAMPLE WT:     0.4752 g
STATION NUMBER: 1        EQUIL INTERVAL:     10 sec   FREE SPACE:  55.6636 cc
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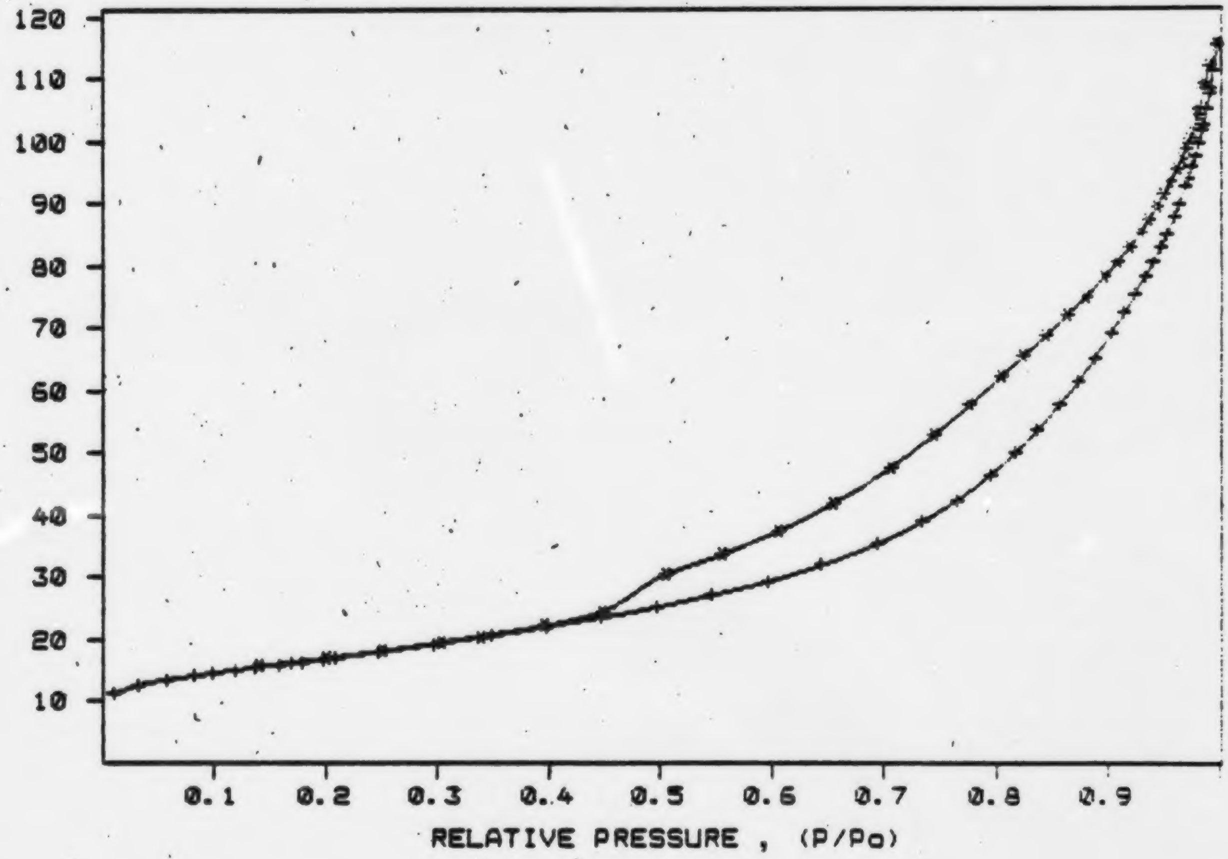
ISOTHERM PLOT
+ ads, * des



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                    Micromeritics Instrument Corporation
SAP 2400 V2.00                                                     PAGE  5

SAMPLE DIRECTORY/NUMBER: DATA1   /147              START 15:11:20 02/03/88
SAMPLE ID: ES2   MAL 227  B5                       COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:47:38 02/04/88
OPERATOR: TK                                       SAMPLE WT:     0.4752 g
STATION NUMBER: 1       EQUIL INTERVAL:    10 sec  FREE SPACE:  55.6636 cc

                         BET SURFACE AREA REPORT

     BET SURFACE AREA:               59.3084  +/-    0.2216   sq. m/g
     SLOPE:                         0.073075 +/-    0.000270
     Y-INTERCEPT:                   0.000324 +/-    0.000049
     C:                           226.495544
     VM:                           13.624087 cc/g STP
     CORRELATION COEFFICIENT: 9.99980E-01

         RELATIVE            VOL ADSORBED                 1/
         PRESSURE             (cc/g STP)           [VA(Po/P - 1)]

          0.0580               13.4168               0.004588
          0.0990               14.4968               0.007579
          0.1588               15.8721               0.011893
          0.1984               16.7627               0.014766
          0.2979               19.1669               0.022139
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              Micromeritics Instrument Corporation
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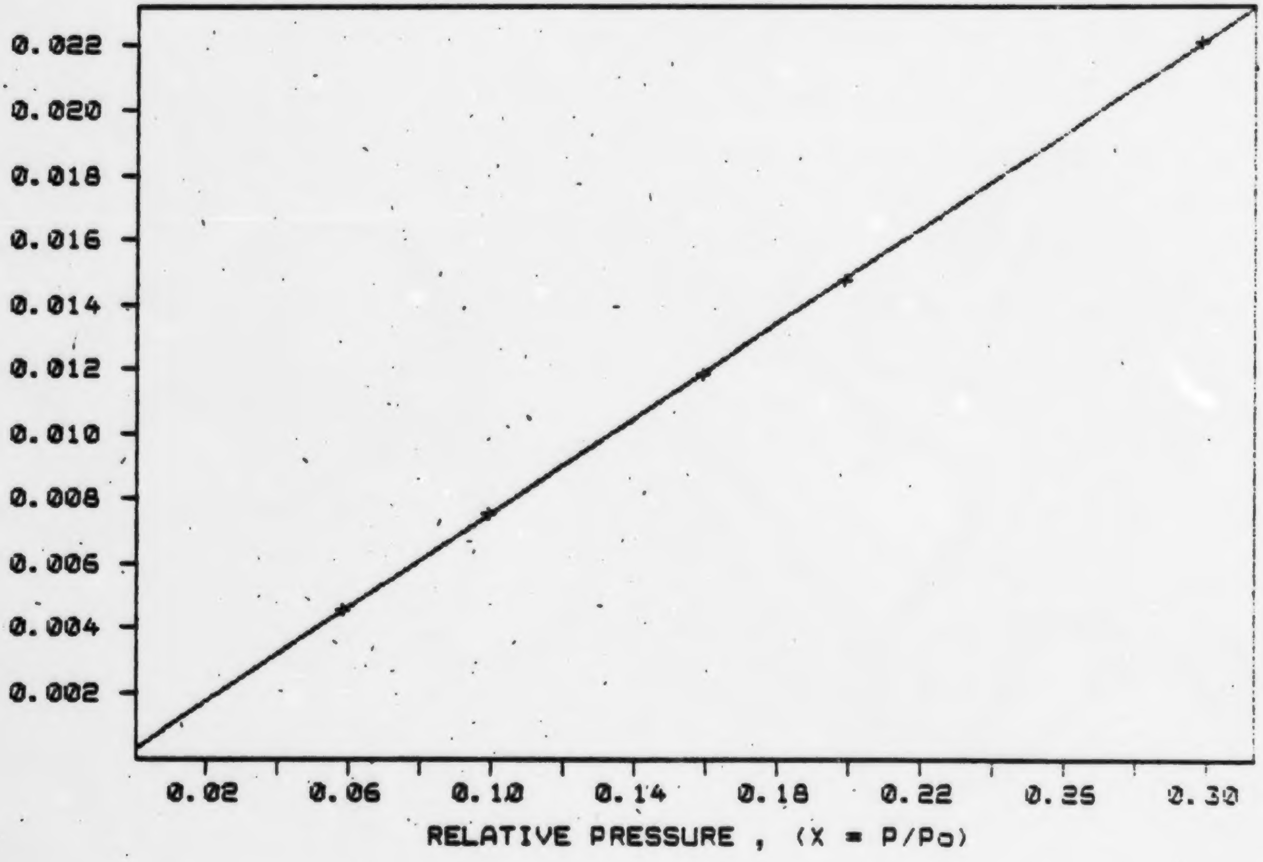
AMPLE DIRECTORY/NUMBER: DATA1   /147          START 15:11:20 02/03/88
AMPLE ID: ES2   MAL 227  B5                   COMPL 02:27:41 02/04/88
UBMITTER: ONTARIO RESEARCH                    REPRT 08:47:38 02/04/88
PERATOR: TK                                   SAMPLE WT:    0.4752 g
TATION NUMBER: 1       EQUIL INTERVAL:    10 sec   FREE SPACE:  55.6636 cc
```

BET PLOT



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                  Micromeritics Instrument Corporation
ASAP 2400 V2.00
                                                                  PAGE  7

SAMPLE DIRECTORY/NUMBER: DATA1    /147
SAMPLE ID: ES2    MAL 227  B5      -               START 15:11:20 02/03/88
SUBMITTER: ONTARIO RESEARCH                        COMPL 02:27:41 02/04/88
OPERATOR: TK                                       REPRT 08:47:38 02/04/88
                                                   SAMPLE WT:     0.4752 g
STATION NUMBER: 1      EQUIL INTERVAL:    10 sec   FREE SPACE:   55.6636 cc

                        LANGMUIR SURFACE AREA REPORT

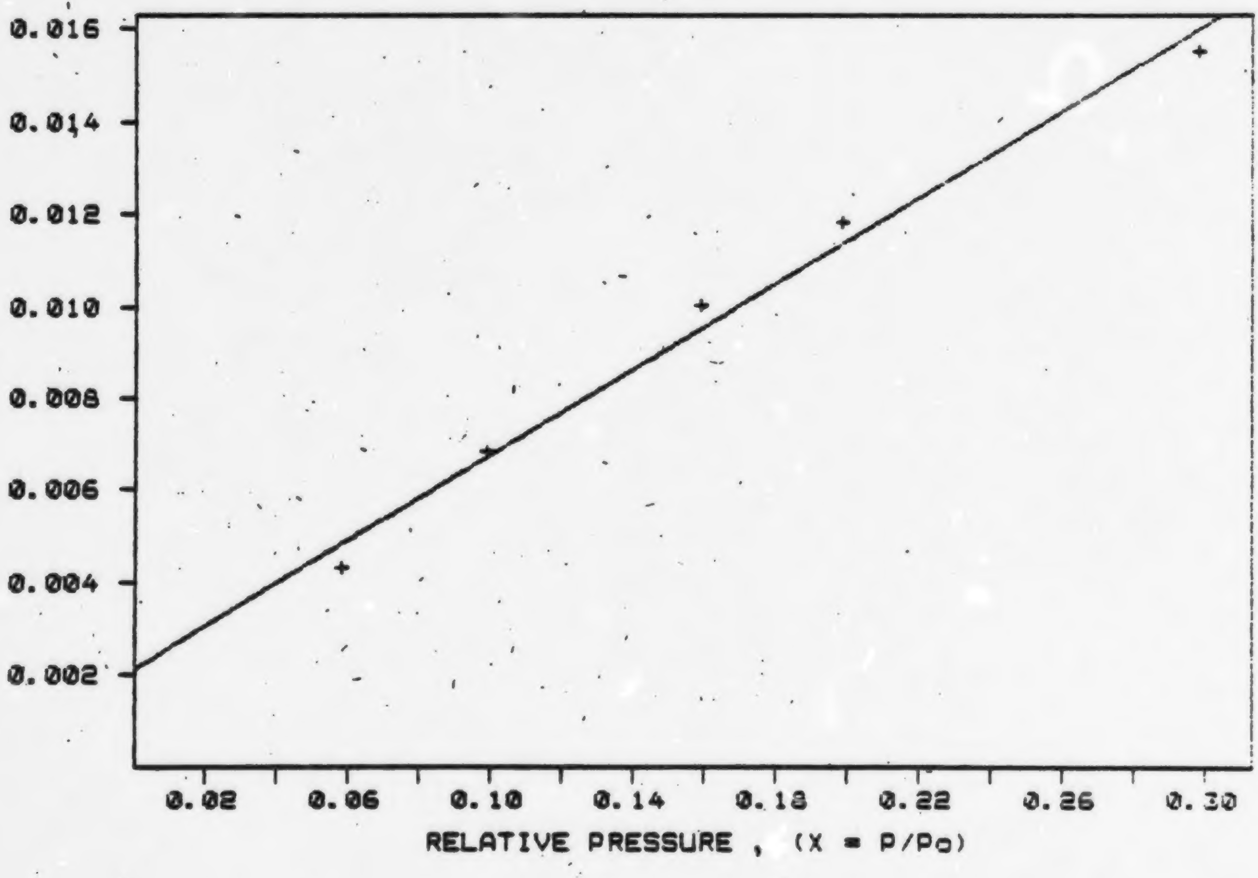
      LANGMUIR SURFACE AREA:       93.4709    +/-     5.9918   sq. m/g
      SLOPE:                        0.046573 +/-     0.002985
      Y-INTERCEPT:                  0.002143 +/-     0.000545
      C:                           21.736517
      VM:                          21.471764 cc/g STP
      CORRELATION COEFFICIENT: 9.93893E-01

         RELATIVE              VOL ADSORBED                1/
         PRESSURE              (cc/g STP)              [VA*Po/P]

          0.0580                 13.4168                0.004322
          0.0990                 14.4968                0.006829
          0.1588                 15.8721                0.010004
          0.1984                 16.7627                0.011836
          0.2979                 19.1669                0.015543
```

```
AMPLE DIRECTORY/NUMBER: DATA1   /147              START 15:11:20 02/03/88
AMPLE ID: ES2   MAL 227  B5                       COMPL 02:27:41 02/04/88
UBMITTER: ONTARIO RESEARCH                        REPRT 08:47:38 02/04/88
PERATOR: TK                                       SAMPLE WT:     0.4752 g
TATION NUMBER: 1        EQUIL INTERVAL:    10 sec FREE SPACE:  55.6636 cc
```

LANGMUIR PLOT



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                     Micromeritics Instrument Corporation
SAP 2400 V2.00                                                         PAGE  9

A[illegible]PLE DIRECTORY/NUMBER: DATA1    /147       START 15:11:20 02/03/88
AMPLE ID: ES2    MAL 227  B5                      COMPL 02:27:41 02/04/88
U[illegible]MITTER: ONTARIO RESEARCH                         RERRT 08:47:38 02/04/88
P[illegible]RATOR: TK                                        SAMPLE WT:     0.4752 g
TATION NUMBER: 1        EQUIL INTERVAL:    10 sec  FREE SPACE:  55.6636 cc

                  BJH ADSORPTION PORE DISTRIBUTION REPORT

PORE DIAMETER      AVERAGE   INCREMENTAL  CUMULATIVE   INCREMENTAL  CUMULATIVE
   RANGE          DIAMETER   PORE VOLUME  PORE VOLUME   PORE AREA    PORE AREA
    (A )            (A )       (cc/g)       (cc/g)      (sq. m/g)    (sq. m/g)

6[illegible]37.3-  2470.0     2969.8     0.006547     0.006547       0.088        0.088
2[illegible]70.0-  1950.7     2149.2     0.004636     0.011182       0.086        0.174
1950.7-  1890.4     1919.6     0.001523     0.012705       0.032        0.206
1[illegible]90.4-  1505.2     1653.8     0.003680     0.016385       0.089        0.295
1[illegible]05.2-  1256.7     1358.2     0.003895     0.020280       0.115        0.410
1256.7-  1160.4     1204.6     0.001820     0.022099       0.060        0.470
1[illegible]60.4-   974.1     1050.6     0.003499     0.025599       0.133        0.604
 [illegible]74.1-   876.8      920.2     0.002819     0.028417       0.123        0.726
 876.8-   760.4      810.0     0.003245     0.031662       0.160        0.886
 760.4-   679.5      715.2     0.002980     0.034642       0.167        1.053
 [illegible]79.5-   626.4      650.7     0.002188     0.036830       0.135        1.187
 [illegible]26.4-   529.2      569.3     0.005058     0.041889       0.355        1.543
 529.2-   477.2      500.4     0.003804     0.045692       0.304        1.847
 [illegible]77.2-   413.0      440.2     0.004747     0.050439       0.431        2.278
 [illegible]13.0-   374.1      391.5     0.003696     0.054135       0.378        2.656
 374.1-   333.9      351.6     0.004316     0.058451       0.491        3.147
 333.9-   301.8      316.1     0.004490     0.062941       0.568        3.715
 301.8-   267.5      282.4     0.005374     0.068315       0.761        4.476
 267.5-   238.7      251.4     0.005593     0.073908       0.890        5.366
 238.7-   213.1      224.3     0.005774     0.079682       1.030        6.396
 213.1-   184.8      196.8     0.008137     0.087819       1.654        8.050
 184.8-   163.9      173.0     0.007505     0.095325       1.735        9.785
 163.9-   146.7      154.2     0.007005     0.102330       1.817       11.602
 146.7-   129.2      136.7     0.008293     0.110623       2.426       14.028
 129.2-   115.4      121.4     0.007635     0.118258       2.515       16.544
 115.4-   103.6      108.8     0.007070     0.125328       2.599       19.143
 103.6-    90.7       96.2     0.008205     0.133534       3.412       22.555
  90.7-    79.9       84.5     0.007238     0.140771       3.426       25.981
  79.9-    69.3       73.7     0.007146     0.147917       3.877       29.858
  69.3-    59.2       63.3     0.006480     0.154398       4.093       33.952
  59.2-    51.5       54.8     0.004821     0.159219       3.522       37.474
  51.5-    45.3       47.9     0.003589     0.162808       2.994       40.468
  45.3-    40.1       42.3     0.002968     0.165776       2.805       43.273
  40.1-    35.8       37.6     0.002407     0.168183       2.558       45.831
  35.8-    32.0       33.6     0.002020     0.170203       2.402       48.232
  32.0-    28.8       30.2     0.001905     0.172108       2.524       50.756
  28.8-    25.7       27.1     0.001750     0.173858       2.588       53.344
  25.7-    23.0       24.2     0.001295     0.175153       2.143       55.488
  23.0-    21.0       21.9     0.000613     0.175767       1.121       56.608
  21.0-    20.5       20.8     0.000122     0.175888       0.235       56.843
  20.5-    19.5       20.0     0.000162     0.176051       0.324       57.168
```

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                  Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                       PAGE 10

SAMPLE DIRECTORY/NUMBER: DATA1    /147              START 15:11:20 02/03/88
SAMPLE ID: ES2    MAL 227  B5                       COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                         REPRT 08:47:38 02/04/88
OP RATOR: TK                                        SAMPLE WT:     0.4752 g
STATION NUMBER: 1        EQUIL INTERVAL:    10 sec  FREE SPACE:  55.6636 cc

                  BJH ADSORPTION PORE DISTRIBUTION REPORT

 PORE DIAMETER     AVERAGE   INCREMENTAL  CUMULATIVE   INCREMENTAL  CUMULATIVE
    RANGE          DIAMETER  PORE VOLUME  PORE VOLUME  PORE AREA    PORE AREA
     (A )            (A )      (cc/g)       (cc/g)     (sq. m/g)    (sq. m/g)

  19.5-    18.6      18.8     0.000176     0.176227      0.375        57.543
  18.6-    17.5      18.0     0.000060     0.176287      0.134        57.677
```

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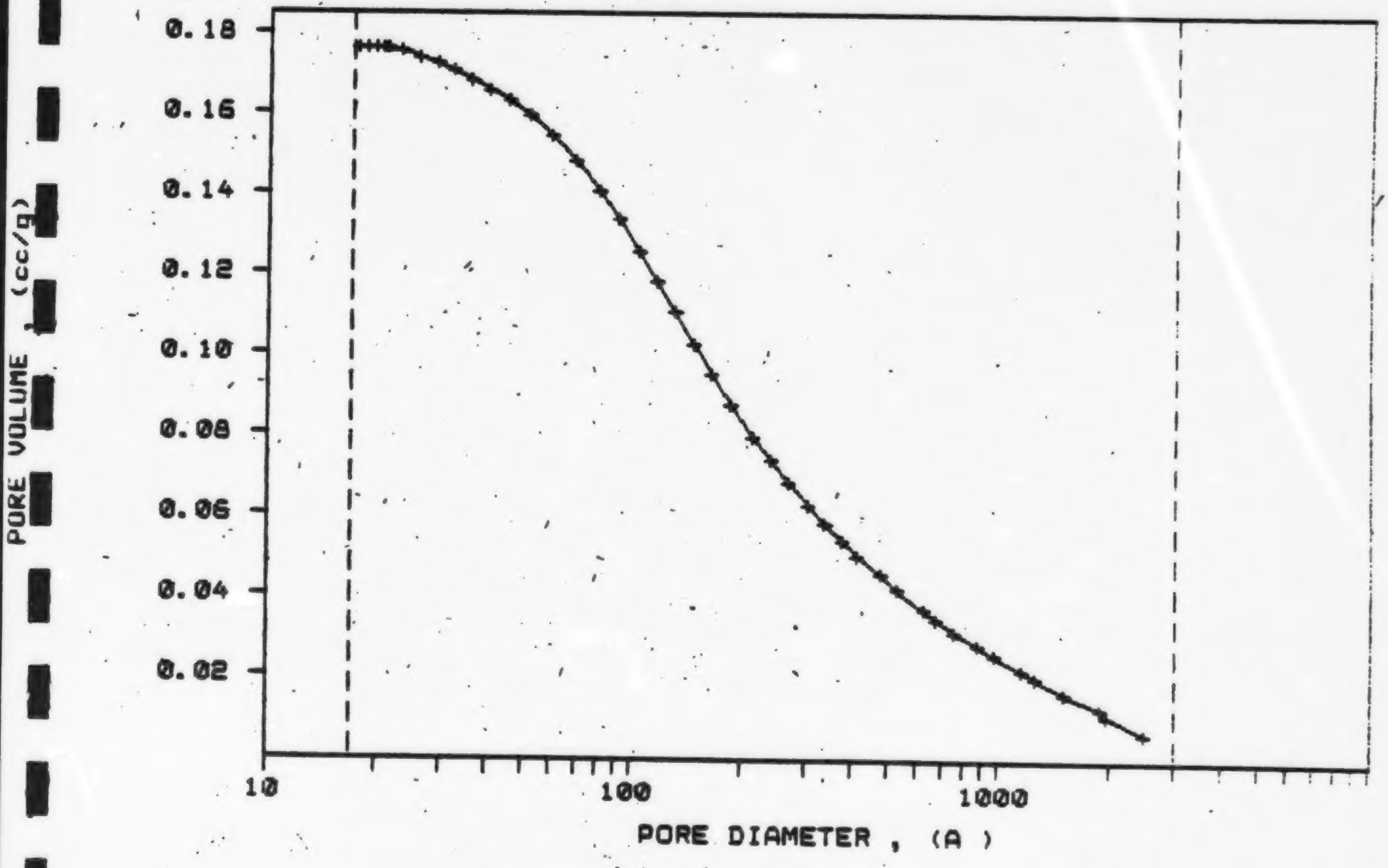
SAMPLE DIRECTORY/NUMBER: DATA1 /147
SAMPLE ID: ES2 MAL 227 B5
SUBMITTER: ONTARIO RESEARCH
OPERATOR: TK
STATION NUMBER: 1 EQUIL INTERVAL: 10 sec

START 15:11:20 02/03/88
COMPL 02:27:41 02/04/88
REPRT 08:47:38 02/04/88
SAMPLE WT: 0.4752 g
FREE SPACE: 55.6636 cc

CUMULATIVE ADSORPTION PORE VOLUME PLOT



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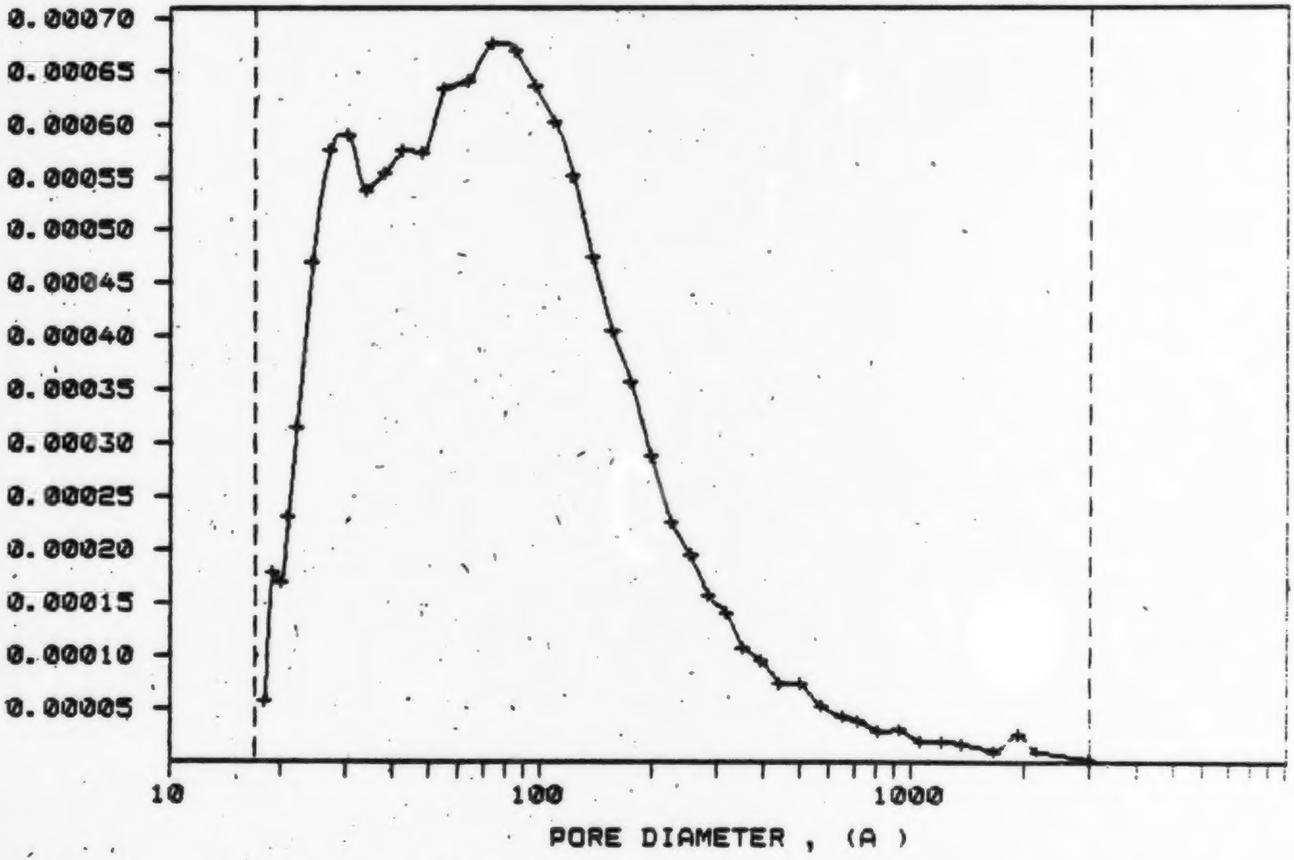
                    Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                    PAGE 12

SAMPLE DIRECTORY/NUMBER: DATA1    /147              START 15:11:20 02/03/88
SAMPLE ID: ES2    MAL 227  B5                       COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                         REPRT 08:47:38 02/04/88
OPERATOR: TK                                        SAMPLE WT:     0.4752 g
STATION NUMBER: 1          EQUIL INTERVAL:    10 sec  FREE SPACE:  55.6636 cc
```

dV/dD ADSORPTION PORE VOLUME PLOT



Micromeritics Instrument Corporation

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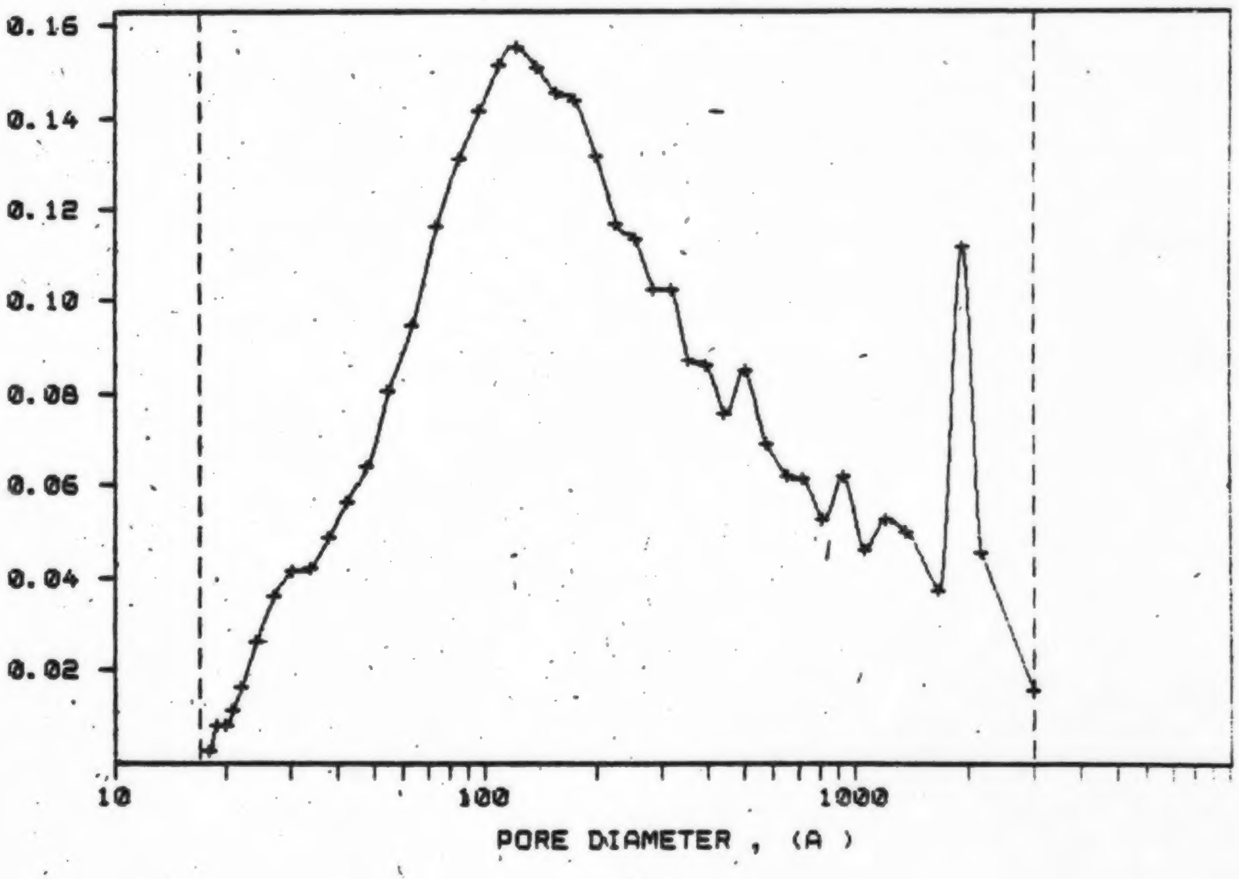
SA PLE DIRECTORY/NUMBER: DATA1 /147
SAMPLE ID: ES2 MAL 227 B5
SUBMITTER: ONTARIO RESEARCH
O RATOR: TK
ST TION NUMBER: 1 EQUIL INTERVAL: 10 sec

START 15:11:20 02/03/88
COMPL 02:27:41 02/04/88
REPRT 08:47:38 02/04/88
SAMPLE WT: 0.4752 g
FREE SPACE: 55.6636 cc

dV/dlog(D) ADSORPTION PORE VOLUME PLOT



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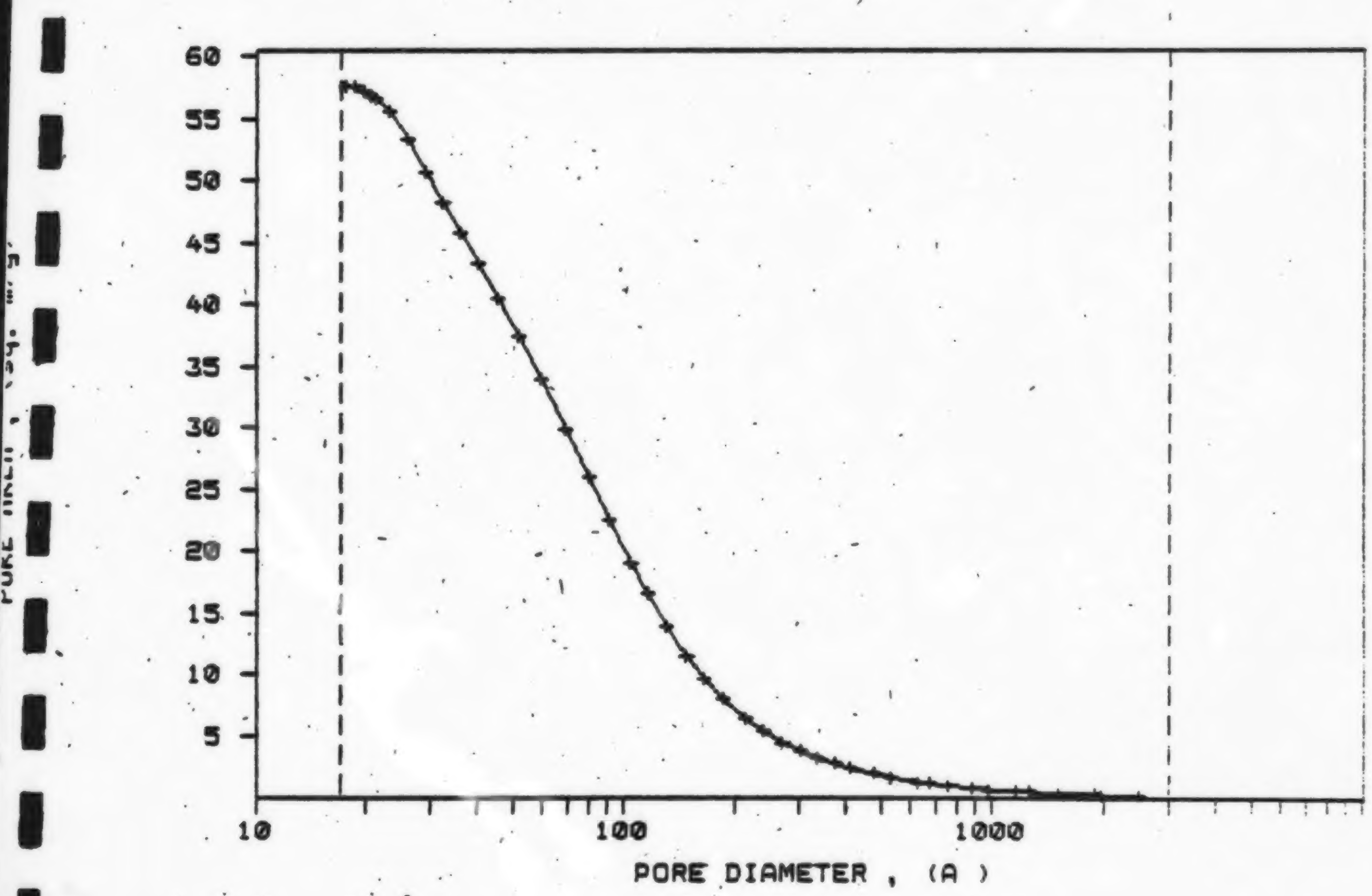
                Micromeritics Instrument Corporation
SAP 2400 V2.00                                                      PAGE 14

SAMPLE DIRECTORY/NUMBER: DATA1    /147           START 15:11:20 02/03/88
SAMPLE ID: ES2    MAL 227  B5                    COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                      REPRT 08:47:38 02/04/88
OPERATOR: TK                                     SAMPLE WT:      0.4752 g
STATION NUMBER: 1        EQUIL INTERVAL:    10 sec   FREE SPACE:  55.6636 cc
```

CUMULATIVE ADSORPTION PORE AREA PLOT



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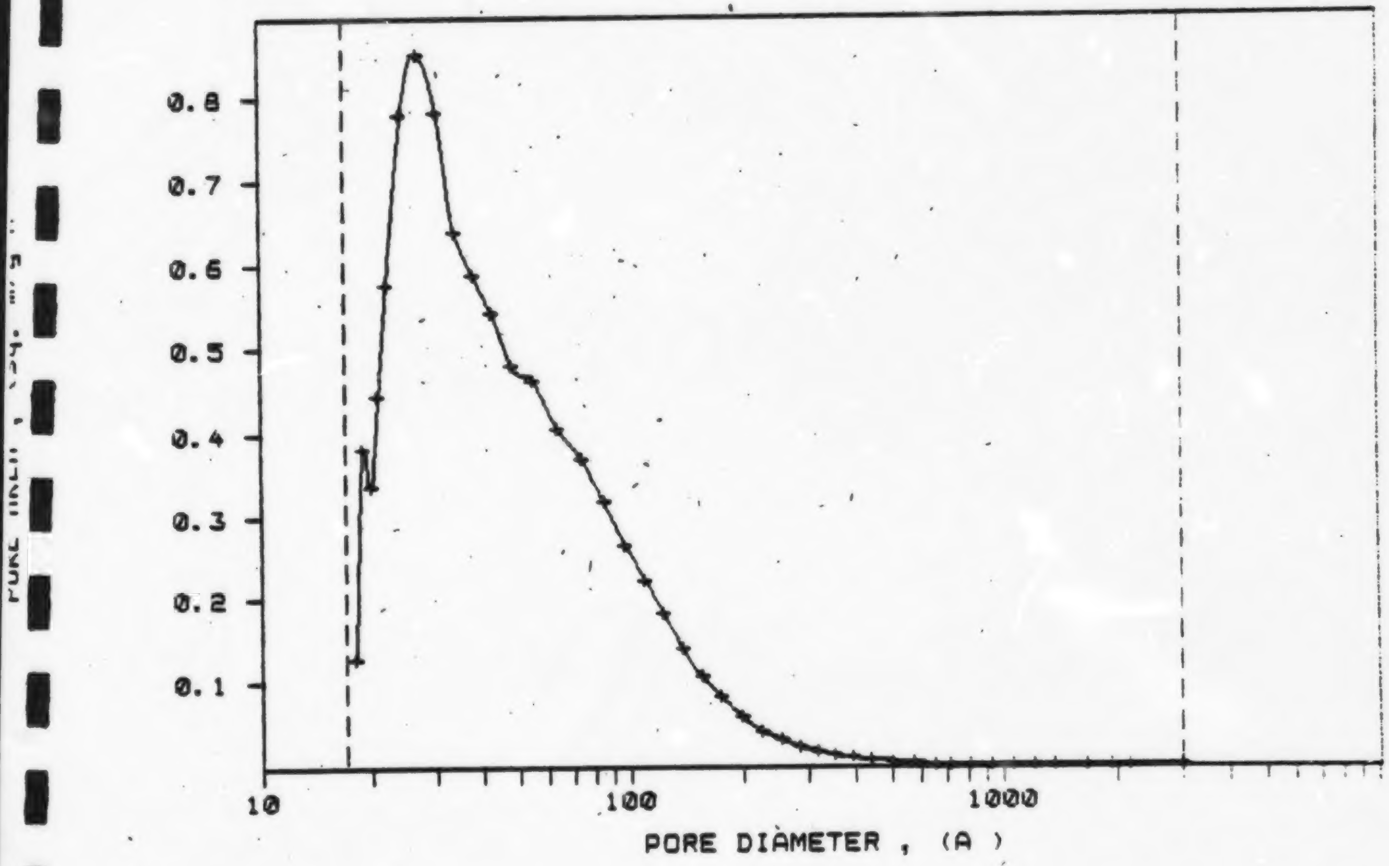
                    Micromeritics Instrument Corporation
SAP 2400 V2.00                                                   PAGE 15

SAMPLE DIRECTORY/NUMBER: DATA1    /147             START 15:11:20 02/03/88
SAMPLE ID: ES2    MAL 227  B5                      COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:47:38 02/04/88
OPERATOR: TK                                       SAMPLE WT:     0.4752 g
STATION NUMBER: 1       EQUIL INTERVAL:    10 sec  FREE SPACE:  55.6636 cc
```

dA/dD ADSORPTION PORE AREA PLOT



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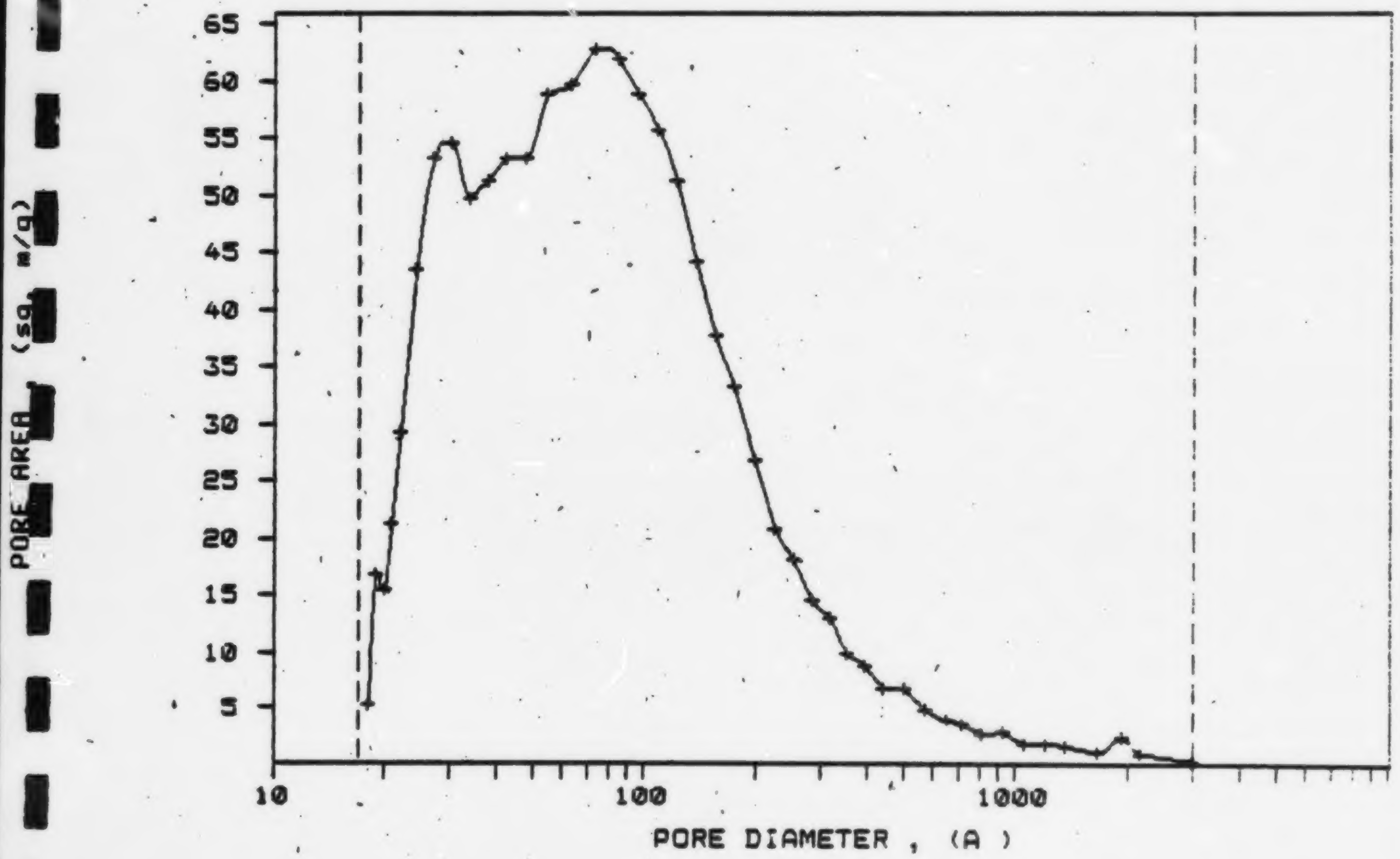
                    Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                    PAGE 16

SAMPLE DIRECTORY/NUMBER: DATA1    /147             START 15:11:20 02/03/88
SAMPLE ID: ES2   MAL 227  B5                       COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:47:38 02/04/88
OPERATOR: TK                                       SAMPLE WT:     0.4752 g
STATION NUMBER: 1        EQUIL INTERVAL:    10 sec FREE SPACE:  55.6636 cc
```



dA/dlog(D) ADSORPTION PORE AREA PLOT

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                                                                   PAGE 17
SAP 2400 V2.00

AMPLE DIRECTORY/NUMBER: DATA1    /147              START 15:11:20 02/03/88
AMPLE ID: ES2    MAL 227  B5                       COMPL 02:27:41 02/04/88
UBMITTER: ONTARIO RESEARCH                         REPRT 08:47:38 02/04/88
PERATOR: TK                                        SAMPLE WT:    0.4752 g
TATION NUMBER: 1       EQUIL INTERVAL:    10 sec   FREE SPACE:  55.6636 cc

                BJH DESORPTION PORE DISTRIBUTION REPORT

PORE DIAMETER     AVERAGE    INCREMENTAL CUMULATIVE  INCREMENTAL CUMULATIVE
   RANGE          DIAMETER   PORE VOLUME PORE VOLUME  PORE AREA   PORE AREA
   (A )            (A )        (cc/g)      (cc/g)    (sq. m/g)   (sq. m/g)

1 75.5- 1377.5    1571.2     0.004552    0.004552      0.116       0.116
1 77.5- 1285.2    1328.1     0.001641    0.006192      0.049       0.165
1285.2-  985.7    1095.6     0.005289    0.011481      0.193       0.358
 985.7-  922.3     951.9     0.001608    0.013089      0.068       0.426
  22.3-  779.8     838.8     0.003778    0.016867      0.180       0.606
 779.8-  715.3     744.7     0.002190    0.019057      0.118       0.724
 715.3-  639.2     672.8     0.002760    0.021817      0.164       0.888
  39.2-  575.2     603.7     0.002557    0.024374      0.169       1.057
 575.2-  510.9     539.1     0.003065    0.027439      0.227       1.285
 510.9-  446.0     473.9     0.003767    0.031206      0.318       1.603
  46.0-  393.6     416.4     0.003692    0.034898      0.355       1.957
  93.6-  354.9     372.2     0.003328    0.038226      0.358       2.315
 354.9-  315.0     332.5     0.004009    0.042235      0.482       2.797
  15.0-  283.3     297.4     0.003691    0.045926      0.497       3.294
 283.3-  252.0     265.7     0.004287    0.050213      0.645       3.939
 252.0-  224.5     236.5     0.004184    0.054397      0.708       4.647
 224.5-  198.0     209.4     0.005197    0.059594      0.992       5.639
  98.0-  172.0     183.0     0.006080    0.065673      1.329       6.968
 172.0-  152.4     160.9     0.005496    0.071169      1.366       8.334
 152.4-  134.7     142.4     0.006452    0.077621      1.813      10.146
 134.7-  118.9     125.7     0.007064    0.084684      2.248      12.394
 118.9-  107.4     112.5     0.006523    0.091207      2.319      14.714
 107.4-   94.0      99.7     0.009661    0.100868      3.875      18.589
  94.0-   82.2      87.2     0.010172    0.111040      4.664      23.253
  82.2-   71.3      75.9     0.011253    0.122293      5.931      29.184
  71.3-   60.2      64.7     0.012292    0.134586      7.600      36.783
  60.2-   52.1      55.5     0.009222    0.143808      6.646      43.430
  52.1-   45.4      48.3     0.007521    0.151329      6.234      49.663
  45.4-   40.0      42.3     0.006013    0.157342      5.681      55.345
  40.0-   34.9      37.1     0.014581    0.171922     15.730      71.075
  34.9-   31.0      32.7     0.003092    0.175015      3.783      74.858
  31.0-   27.3      28.9     0.000420    0.175435      0.582      75.440
  27.3-   25.2      26.1     0.000046    0.175481      0.071      75.511
```

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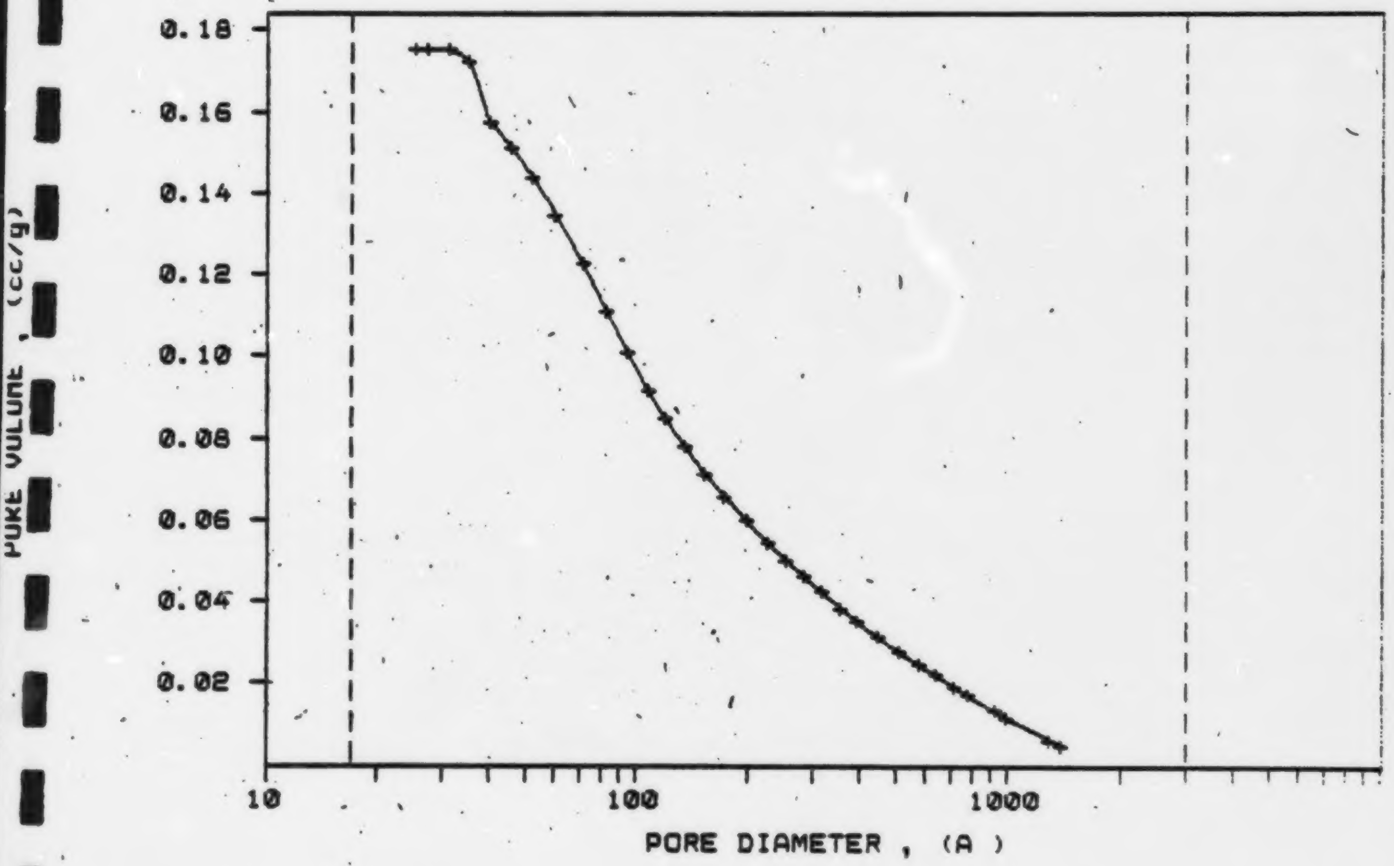
SAMPLE DIRECTORY/NUMBER: DATA1    /147                START 15:11:20 02/03/88
SAMPLE ID: ES2    MAL 227  B5                         COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                           REPRT 08:47:38 02/04/88
OPERATOR: TK                                          SAMPLE WT:     0.4752 g
STATION NUMBER: 1        EQUIL INTERVAL:     10 sec   FREE SPACE:  55.6636 cc
```

CUMULATIVE DESORPTION PORE VOLUME PLOT



Micromeritics Instrument Corporation

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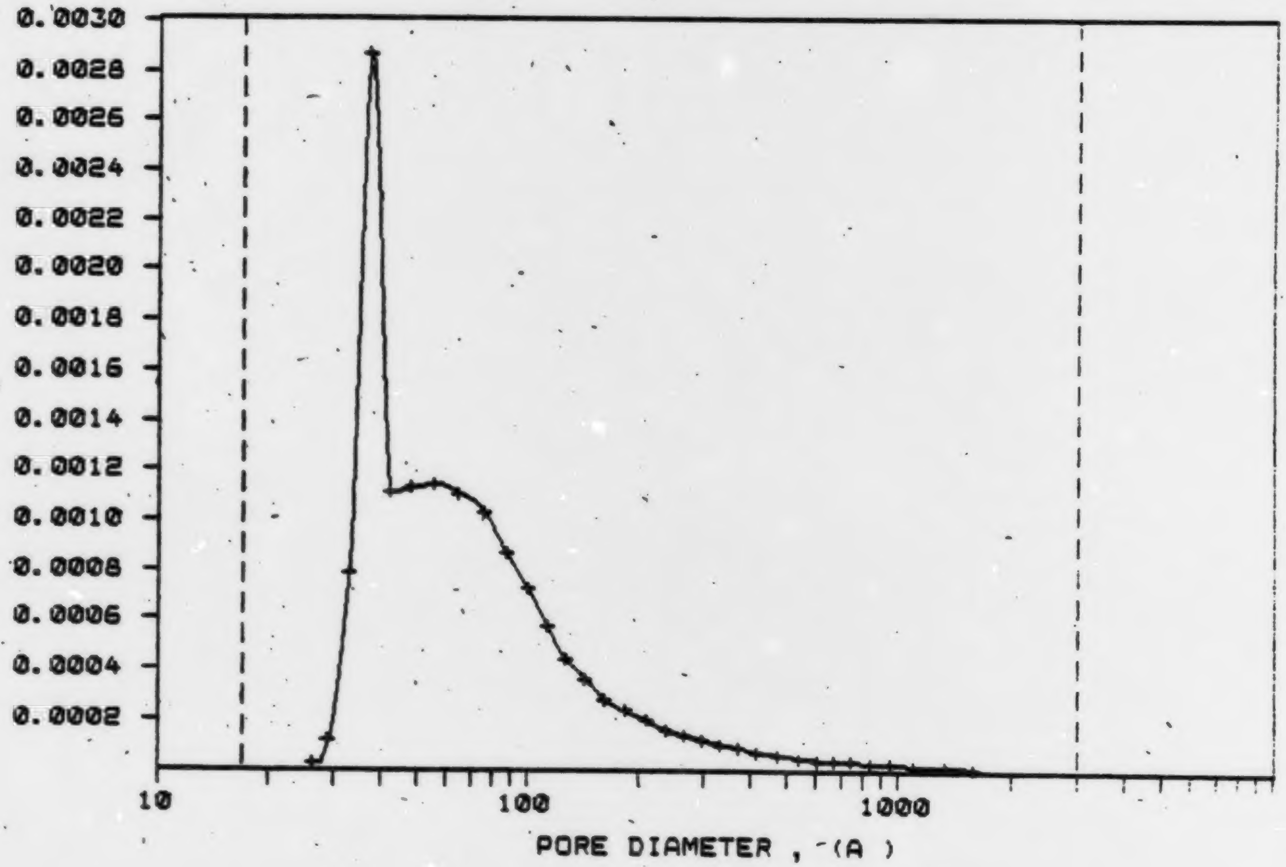
SAMPLE DIRECTORY/NUMBER: DATA1 /147
SAMPLE ID: ES2 MAL 227 B5
SUBMITTER: ONTARIO RESEARCH
OPERATOR: TK
STATION NUMBER: 1 EQUIL INTERVAL: 10 sec

START 15:11:20 02/03/88
COMPL 02:27:41 02/04/88
REPRT 08:47:38 02/04/88
SAMPLE WT: 0.4752 g
FREE SPACE: 55.6636 cc

dV/dD DESORPTION PORE VOLUME PLOT



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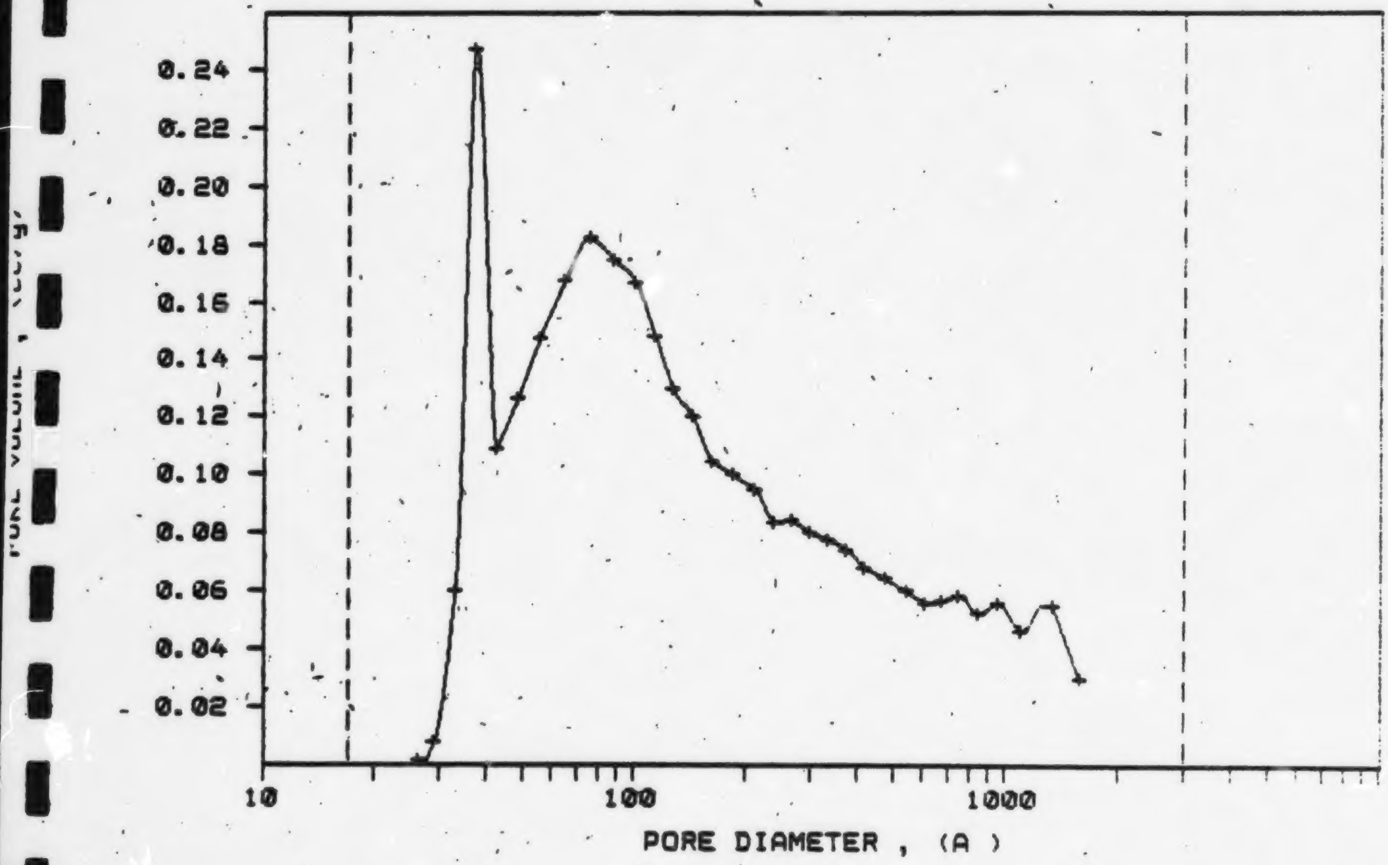
                    Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                        PAGE 20

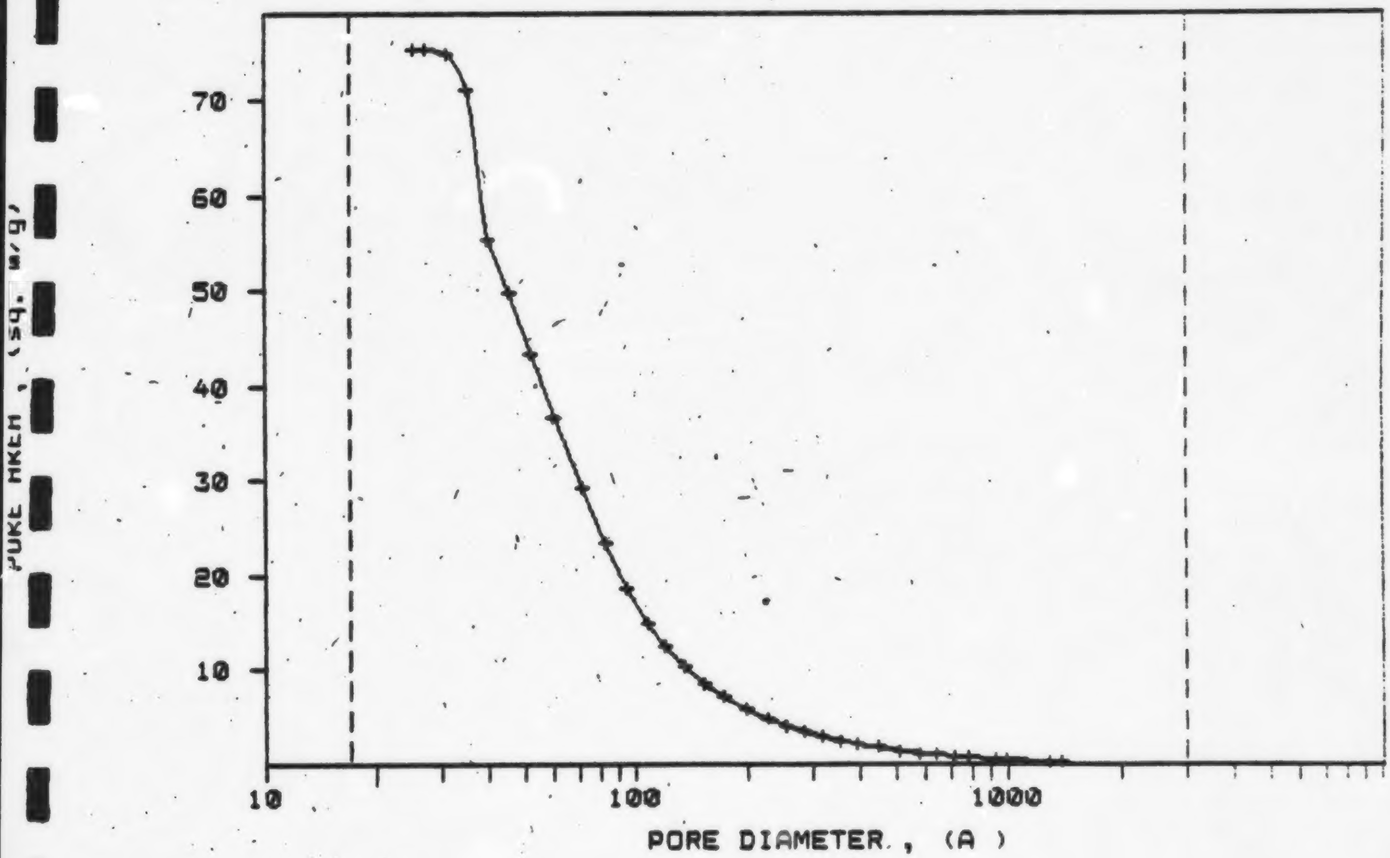
SAMPLE DIRECTORY/NUMBER: DATA1   /147              START 15:11:20 02/03/88
SAMPLE ID: ES2    MAL 227  B5                      COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:47:38 02/04/88
OPERATOR: TK                                       SAMPLE WT:     0.4752 g
STATION NUMBER: 1       EQUIL INTERVAL:    10 sec  FREE SPACE:  55.6636 cc
```

dV/dlog(D) DESORPTION PORE VOLUME PLOT



SAMPLE DIRECTORY/NUMBER: DATA1 /147 START 15:11:20 02/03/88
SAMPLE ID: ES2 MAL 227 B5 COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH REPRT 06:47:38 02/04/88
OPERATOR: TK SAMPLE WT: 0.4752 g
STATION NUMBER: 1 EQUIL INTERVAL: 10 sec FREE SPACE: 55.6636 cc

CUMULATIVE DESORPTION PORE AREA PLOT



Micromeritics Instrument Corporation

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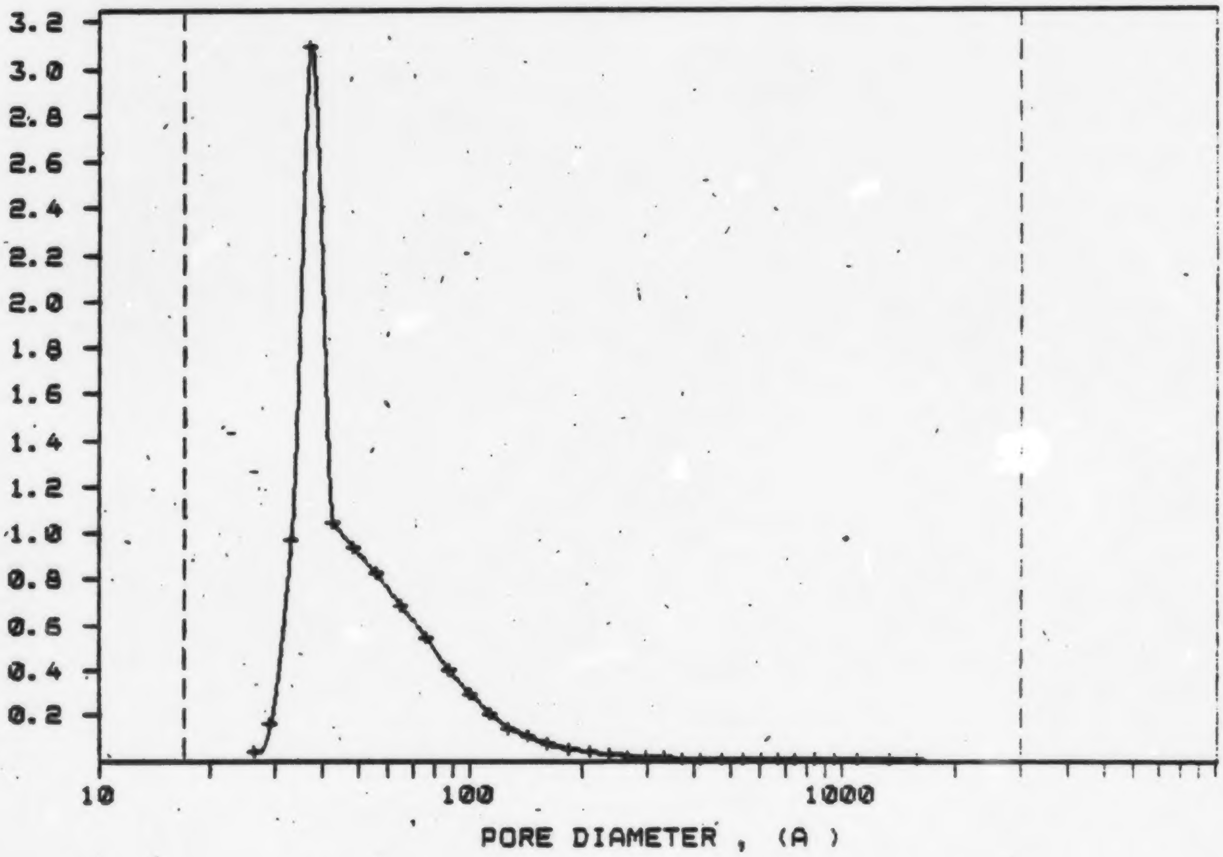
SAMPLE DIRECTORY/NUMBER: DATA1    /147             START 15:11:20 02/03/88
SAMPLE ID: ES2    MAL 227   B5                     COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:47:38 02/04/88
OPERATOR: TK                                       SAMPLE WT:     0.4752 g
STATION NUMBER: 1         EQUIL INTERVAL:   10 sec FREE SPACE:   55.6636 cc
```

dA/dD DESORPTION PORE AREA PLOT



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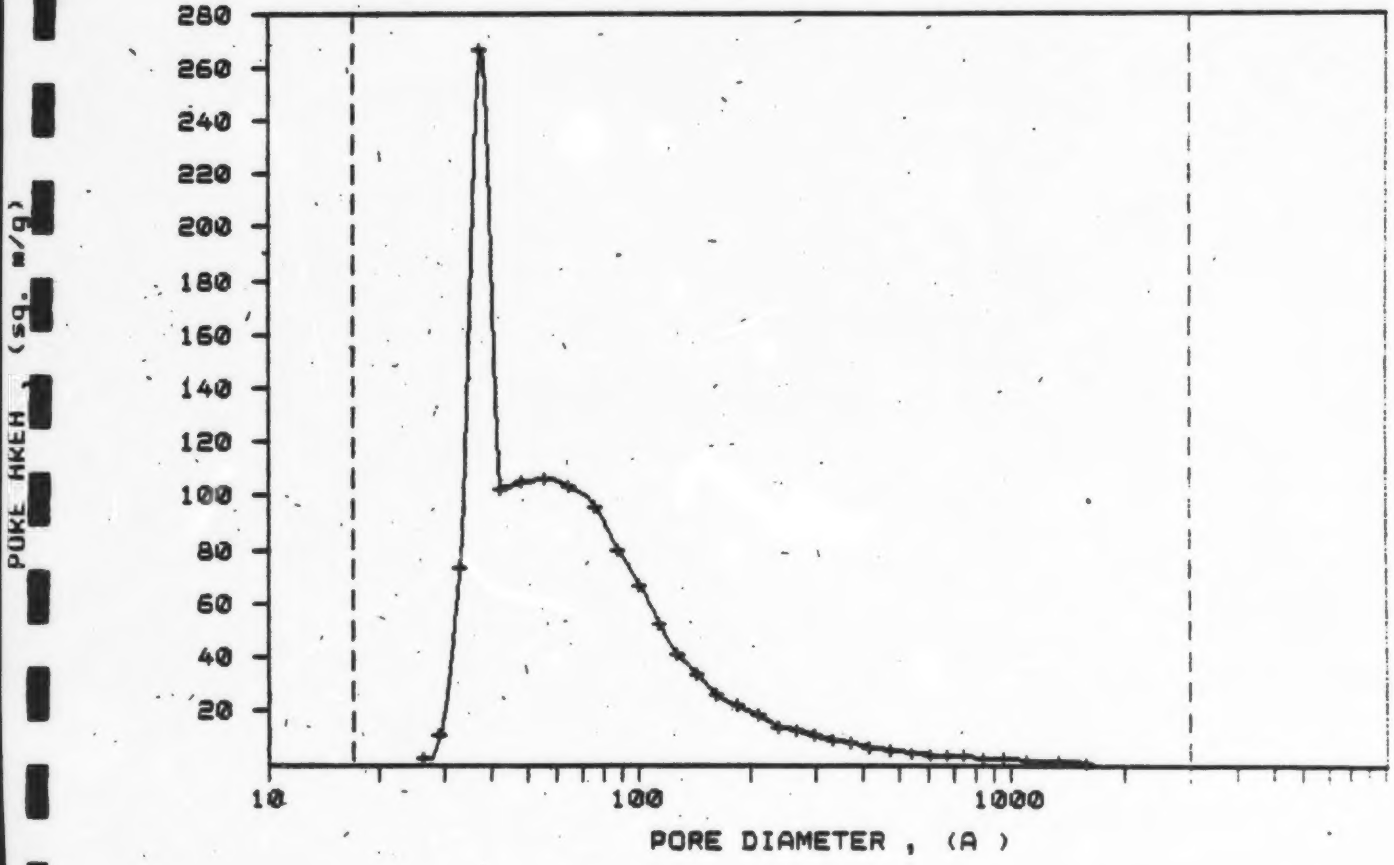
S MPLE DIRECTORY/NUMBER: DATA1    /147             START 15:11:20 02/03/88
SAMPLE ID: ES2    MAL 227  B5                      COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:47:38 02/04/88
O ERATOR: TK                                       SAMPLE WT:     0.4752 g
STATION NUMBER: 1        EQUIL INTERVAL:   10 sec  FREE SPACE:   55.6636 cc
```

dA/dlog(D) DESORPTION PORE AREA PLOT



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                 Micromeritics Instrument Corporation
SAP 2400 V2.00                                                    PAGE  1

A LE DIRECTORY/NUMBER: DATA1    /147           START 15:11:20 02/03/88
AMPLE ID: ES2    MAL 227  B5                   COMPL 02:27:41 02/04/88
U ITTER: ONTARIO RESEARCH                      REPRT 08:47:38 02/04/88
P RATOR: TK                                    SAMPLE WT:     0.4752 g
TATION NUMBER: 1     EQUIL INTERVAL:    10 sec FREE SPACE:   55.6636 cc

                            ANALYSIS LOG

 RELATIVE     PRESSURE    VOL ADSORBED   ELAPSED TIME    SATURATION
 PRESSURE      (mmHg)     (cc/g STP)      (HR:MN)       PRESS.(mmHg)

                                            1:16          751.315
  0.0100        7.545       11.1775         1:51
  0.0325       24.423       12.5371         1:57
  0.0580       43.582       13.4168         2:02
  0.0825       62.024       14.0884         2:08
  0.0990       74.406       14.4968         2:12
  0.1189       89.348       14.9607         2:16
  0.1373      103.182       15.3892         2:20
  0.1588      119.354       15.8721         2:24
  0.1689      126.953       16.1220         2:45
  0.1789      134.486       16.3285         2:51
  0.1984      149.164       16.7627         2:55
  0.2090      157.151       17.0031         2:57
  0.2471      185.779       17.8898         3:00
  0.2979      223.992       19.1669         3:04
  0.3490      262.396       20.5638         3:08
  0.3975      298.920       21.9759         3:13
  0.4473      336.312       23.4793         3:17
                                            3:19          751.936
  0.4968      373.541       25.1436         3:23
  0.5465      410.865       27.0491         3:28
  0.5961      448.107       29.2378         3:32
  0.6445      484.516       31.9214         3:38
  0.6943      521.865       35.3496         3:44
  0.7339      551.628       38.9457         3:50
  0.7656      575.877       42.5172         3:58
  0.7952      597.510       46.5375         4:05
  0.8164      613.412       49.9972         4:13
  0.8366      628.470       53.7501         4:21
  0.8566      643.446       57.8746         4:29
  0.8722      655.097       61.4065         4:37
  0.8872      666.295       65.2293         4:46
  0.9028      677.881       69.4435         4:54
  0.9137      685.972       72.4911         5:02
  0.9233      693.157       75.4777         5:09
  0.9324      699.888       78.3897         5:16
                                            5:20          750.591
  0.9392      704.872       80.8481         5:23
  0.9460      709.856       83.2450         5:30
  0.9512      713.675       85.3172         5:38
  0.9580      718.666       88.0125         5:44
  0.9623      721.725       90.1910         5:52
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                    Micromeritics Instrument Corporation
ASAP 2400 V2.00                                                    PAGE  2

SA PLE DIRECTORY/NUMBER: DATA1   /147              START 15:11:20 02/03/88
SAMPLE ID: ES2   MAL 227  B5                       COMPL 02:27:41 02/04/88
SUBMITTER: ONTARIO RESEARCH                        REPRT 08:47:38 02/04/88
OP RATOR: TK                                       SAMPLE WT:     0.4752 g
ST TION NUMBER: 1       EQUIL INTERVAL:    10 sec  FREE SPACE:  55.6636 cc

                               ANALYSIS LOG

  RELATIVE     PRESSURE     VOL ADSORBED    ELAPSED TIME      SATURATION
  PRESSURE      (mmHg)      (cc/g STP)        (HR:MN)       PRESS.(mmHg)

   0.9683       726.085        93.1249          6:01
   0.9709       727.908        94.4087          6:06
   0.9741       730.185        96.1686          6:12
   0.9776       732.724        98.1026          6:18
   0.9799       734.351        99.7942          6:23
   0.9832       736.694       101.9129          6:30
   0.9845       737.605       103.0219          6:34
   0.9871       739.427       105.4094          6:41
   0.9898       741.315       107.6851          6:47
   0.9901       741.445       108.6314          6:53
   0.9922       742.877       111.5240          7:01
   0.9971       746.456       115.6469          7:05
   0.9902       741.250       112.2854          7:09
   0.9859       737.865       109.4778          7:17
   0.9849       737.019       108.4734          7:21
                                                7:23           748.316
   0.9801       733.375       105.2660          7:30
   0.9787       732.268       104.2989          7:35
   0.9748       729.209       102.0429          7:41
   0.9724       727.387       100.7453          7:47
   0.9690       724.784        99.1212          7:53
   0.9655       722.050        97.6276          7:59
   0.9610       718.601        95.8530          8:06
   0.9551       714.128        93.6961          8:12
   0.9489       709.209        91.6057          8:35
   0.9431       704.807        89.7420          8:41
   0.9356       699.111        87.5207          8:48
   0.9280       693.415        85.4964          8:54
   0.9137       686.360        83.1725          9:01
   0.9083       678.528        80.9249          9:09
   0.8955       668.884        78.1808          9:16
   0.8792       656.586        75.0150          9:23
                                                9:25           746.816
   0.8631       644.546        72.1901          9:32
   0.8445       630.676        68.9417          9:39
   0.8233       614.840        65.4413          9:46
   0.8042       600.561        62.2727          9:54
   0.7761       579.596        57.6762         10:02
   0.7443       555.842        52.8955         10:12
   0.7063       527.441        47.6678         10:20
   0.6550       489.184        41.9005         10:28
   0.6063       452.770        37.4474         10:34
```

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                 Micromeritics Instrument Corporation
P  400 V2.00                                                    PAGE  3

PLE DIRECTORY/NUMBER: DATA1   /147              START 15:11:20 02/03/88
PL  ID: ES2   MAL 227  B5                       COMPL 02:27:41 02/04/88
MI TER: ONTARIO RESEARCH                        REPRT 08:47:38 02/04/88
RATOR: TK                                       SAMPLE WT:    0.4752 g
TI N NUMBER: 1       EQUIL INTERVAL:    10 sec  FREE SPACE:  55.6636 cc

                             ANALYSIS LOG

RE ATIVE     PRESSURE     VOL ADSORBED     ELAPSED TIME      SATURATION
PRESSURE      (mmHg)      (cc/g STP)         (HR:MN)       PRESS.(mmHg)

0.5555       414.880         33.6500          10:42
0.5049       377.096         30.4506          10:48
0.4479       334.503         24.4807          10:57
0.3959       295.682         22.1091          11:02
0.3396       253.589         20.4348          11:05
0.3039       226.972         19.4619          11:08
0.2510       187.463         18.1026          11:11
0.2005       149.749         16.8909          11:14
0.1402       104.676         15.5581          11:17
```

APPENDIX II: Chemical Assay Bulk Samples

Chemical Assay Bulk Samples

	3:1 Float Tails	Caustic Leach Tails	Caustic/Soda Ash Tails
SiO_2	49.69%	44.26%	42.48%
Al_2O_3	24.57	22.38	22.60
Fe_2O_3	10.03	9.10	9.19
CaO	2.19	2.36	2.03
MgO	1.31	1.38	1.24
Na_2O	0.74	7.60	8.88
K_2O	1.67	0.95	0.28
TiO_2	3.40	3.08	3.10
MnO	0.20	0.19	0.18
P_2O_5	0.27	0.23	0.22
V	2.6	.33	0.28
Ba	983 ppm	700 ppm	714 ppm
Sr	472	425	429
Zr	822	741	770
Be	5	5	5
Co	230	210	210
Cr	330	250	240
Cu	100	100	95
Pb	72	260	270
Ni	8400	8200	8600
Cd	<1	<1	<1
Ag	<1	<1	<1
Mo	650	35	4
Zn	210	190	250